Scientific Opportunities with Photoemission Spectroscopy: Present and Future

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ic/ALSaerial/11-96

Outline

- The big picture
- The leading edge of measurements today
  - some examples
- The future:
  - Spin-Resolved photoemission using TOF analyzer and exchange scattering
  - nm-scale measurements, “nanoARPES”
  - time-resolved photoemission
- The MERLIN beamline

Understanding complex correlated phenomena require sharper and sharper tools

The Big Picture

Grand Challenges
&
Why x-rays

Grand Challenges!!

Energy problem – search for 20 TWatts of energy,

solar energy, hydrogen fuel, nuclear energy ??

Membrane Proteins – from 3D structure of Macromolecules to understanding functions-dynamics (engineering of drugs)

Understanding Emergent Phenomena -

Nanoscale materials, Strongly correlated electron systems

(high Tc superconductor……)

The ultra-small - imaging of single atom in a host of others, manipulation of single spin + …

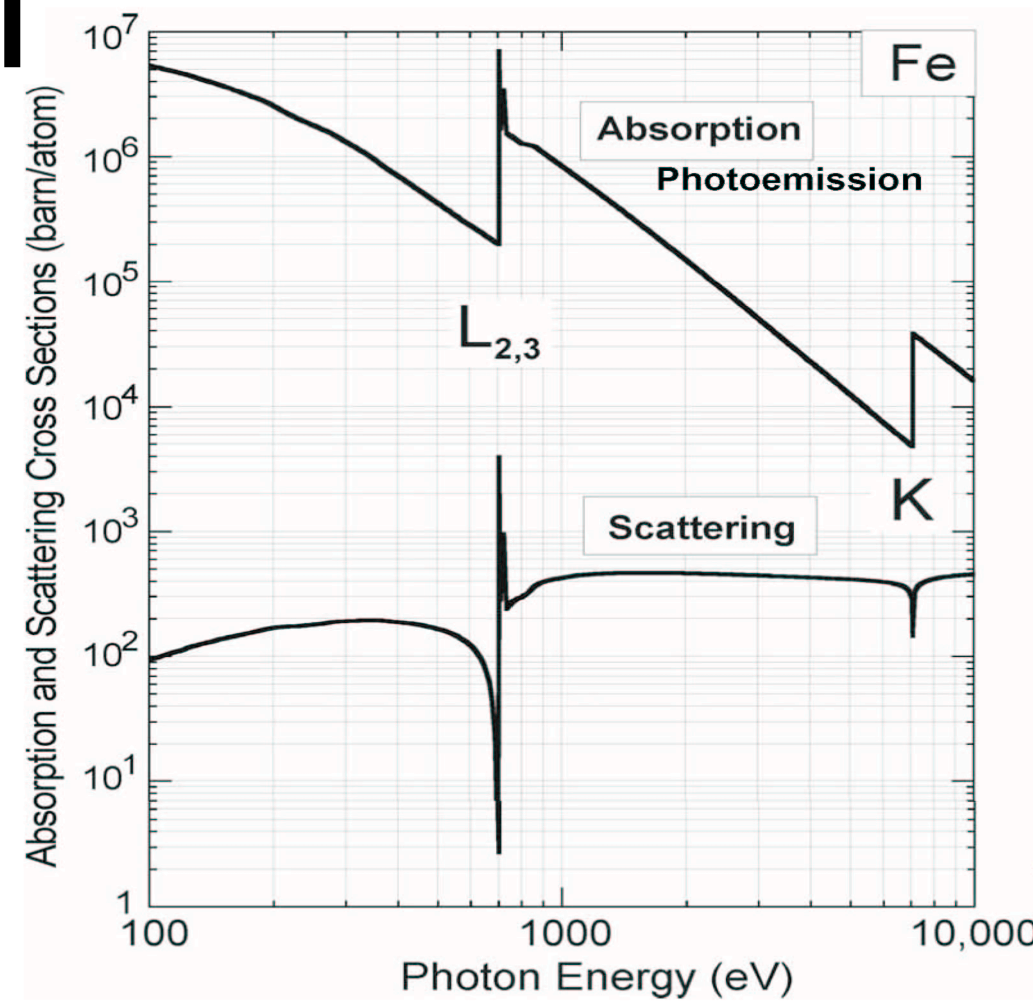
The ultra-fast – science in the ps-fs-as

Why X-Rays (& not neutrons or electrons) ?

Tunable x-rays offer variable interaction cross section

Optical

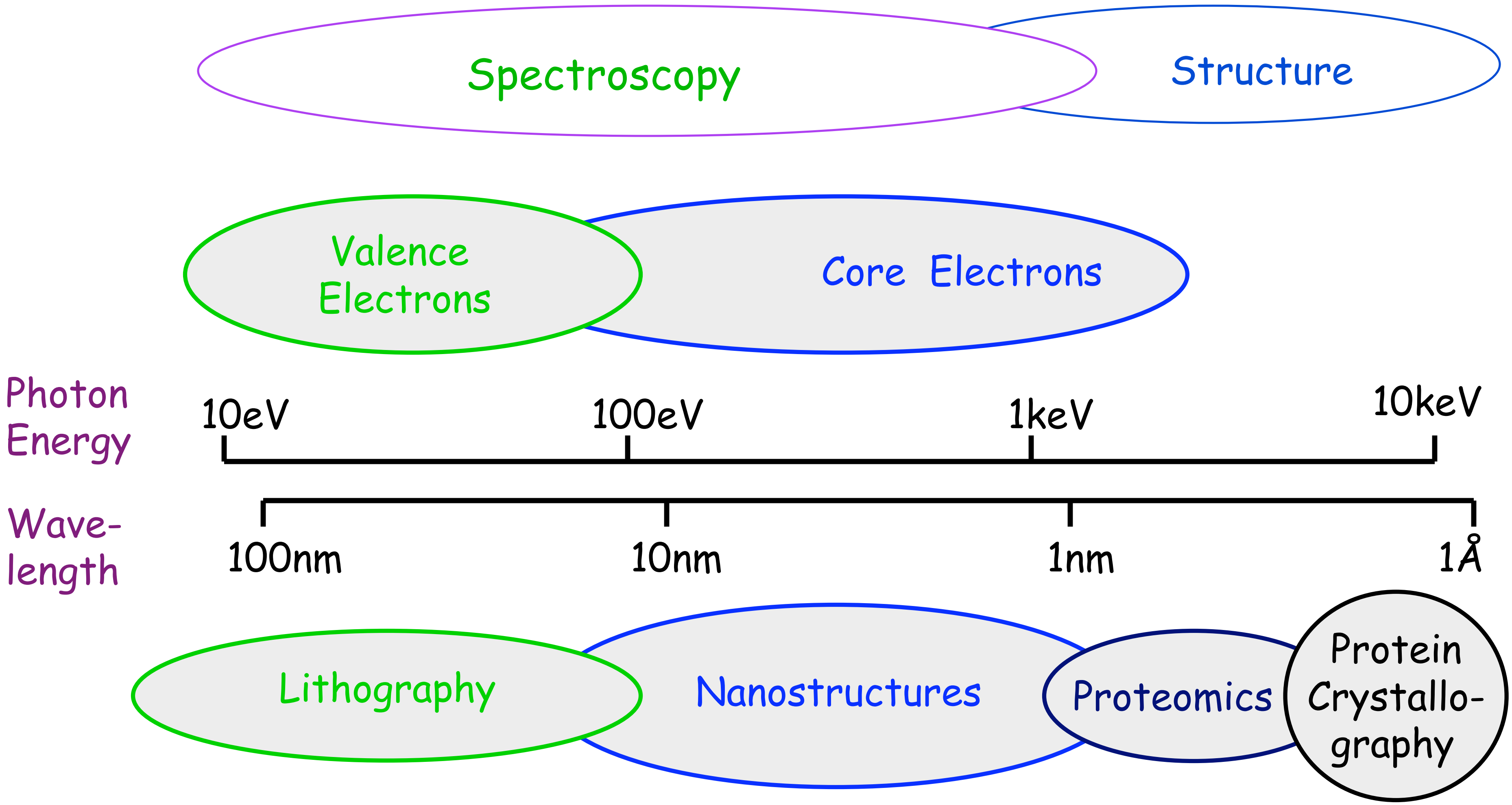
Electrons



neutrons

courtesy: Jo Stohr

Science with Light Sources



Adopted from: Franz Himpsel, CMMP '07

Emergent Phenomena

—

Strongly Correlated electron Systems

Strongly Correlated Electronic Systems

Condensed matter physics

Rich and Novel Electronic Phenomena

Unconventional Superconductivity
- Non-S-wave
- Broken T-Reversal Symmetry
- Role of Bosonic Excitations

Magnetism
- Ferromagnetism
- Spin liquid
- Antiferromagnetism
- Kondo effects

Electronic Phase separation and Charge order Phenomena
- Charge density waves
- Stripes/Checkerboard order
- Negative - U centers

Superconductivity and magnetism

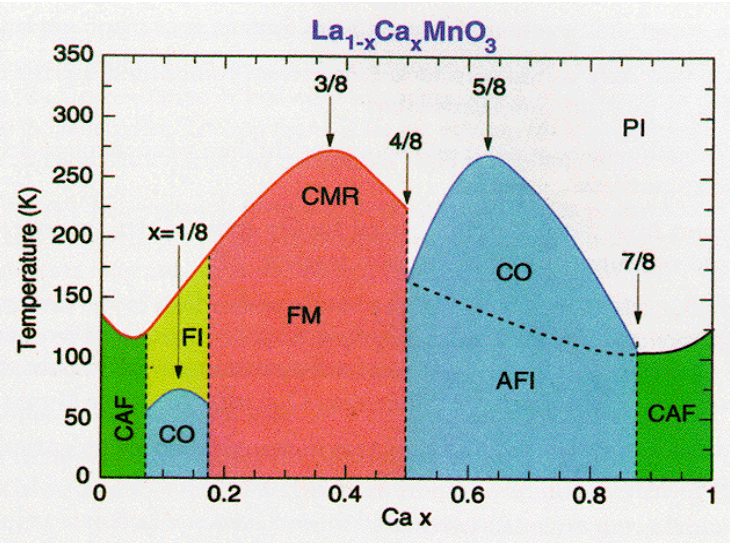
Coupled charge/Spin order

Superconductivity and charge/spin ordered states

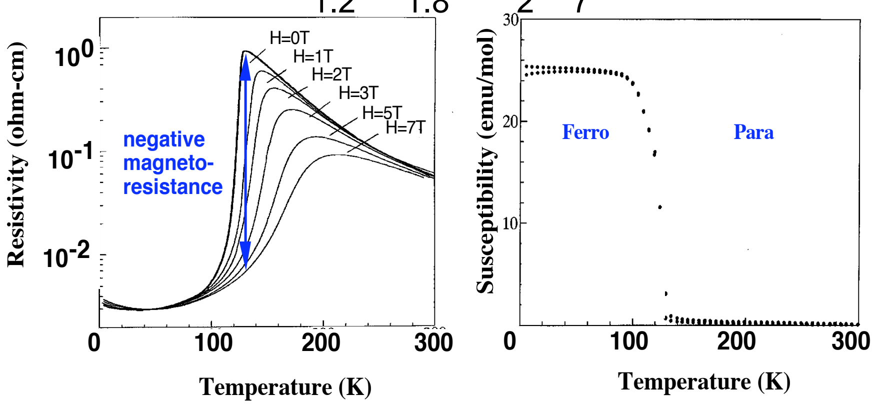
Gap Inhomogeneities

Colossal Magnetoresistance (CMR) Effect

Novel Electronic Phases



$La_{1.2}Sr_{1.8}Mn_2O_7$

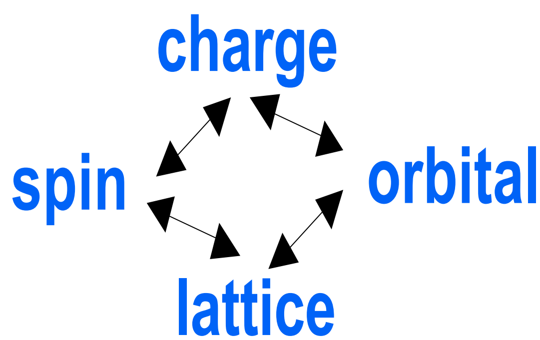


CO :	Charge Order (Stripes)
FI :	Ferromagnetic Insulator
AFI :	Antiferro. Insulator
CAF :	Canted AFM Insulator
CMR :	Colossal MagnetoResis.

- **Large drop of resistivity upon relatively small magnetic fields**
- **Para → Ferromagnetism**
- **Most dramatic on the insulating phase (short range orbital order)**

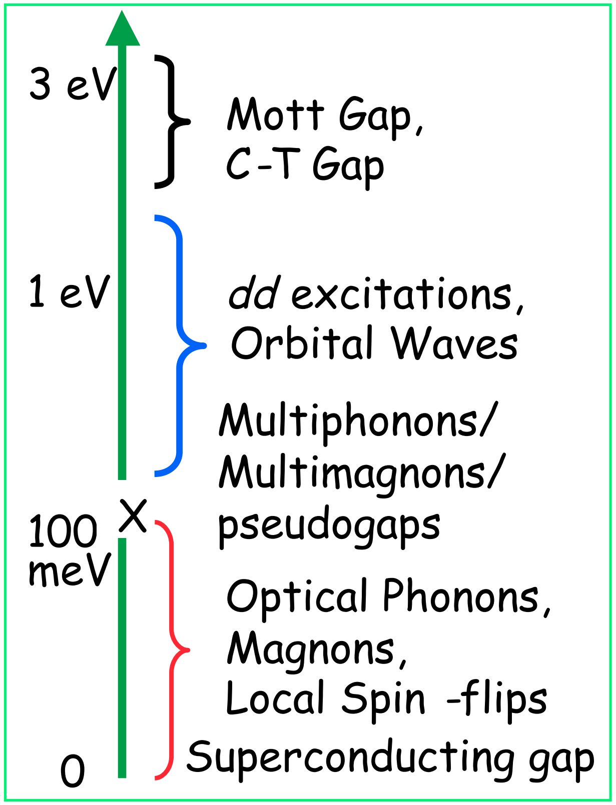
Manganites Exhibit Interplay of Charge, Spin, lattice and Orbital degrees of freedom

Interacting **degrees of freedom (complex electron systems)**



Competition among many *Energy* and *Length* scales Determine the physics of these systems

Energy Scale of Important Excitations



- Superconducting gap ~ 1 – 100meV
- Optical Phonons: ~ 40 - 70 meV
- Magnons: ~ 10 meV - 40 meV
- Pseudogap ~ 30-300 meV
- Multiphonons and multimagnons ~ 50-500 meV
- Orbital fluctuations (originated from optically forbidden d-d excitations): ~ 100 meV - 1.5 eV

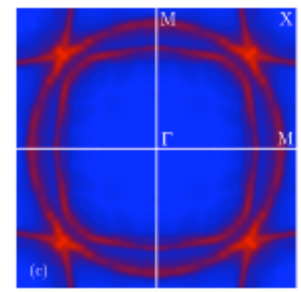
Requirement: High Energy Resolution and High Efficiency Detection

Fundamental Spectroscopies of Condensed Matter

Spectral functions (One-particle properties)
Correlation functions (two-particle properties)

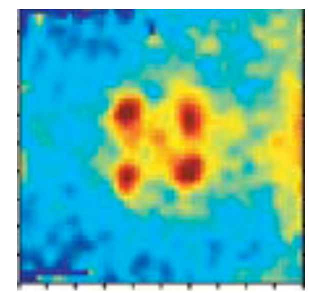
1-particle response

•Angle resolved photoemission (ARPES) :
Single-particle spectrum $A(k,\omega)$

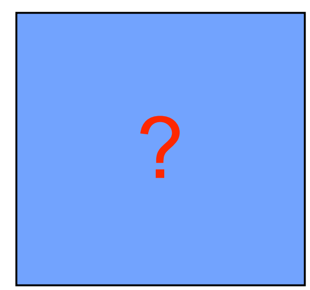


2-particle responses

•<u>*Spin*</u> : Inelastic Neutron Scattering (INS) :
(neutrons carry magnetic moment)
Spin fluctuation spectrum $S(q,\omega)$

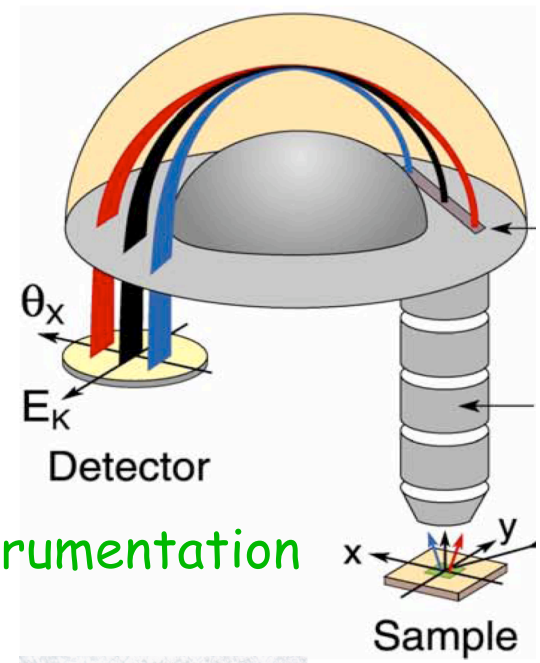


•<u>Charge</u> : Inelastic x-ray scattering (IXS) :
Coupled excitation in the
Charge Channel $N(q,\omega)$

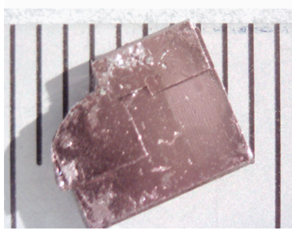


(MERLIN/QERLIN (ALS); FEL)

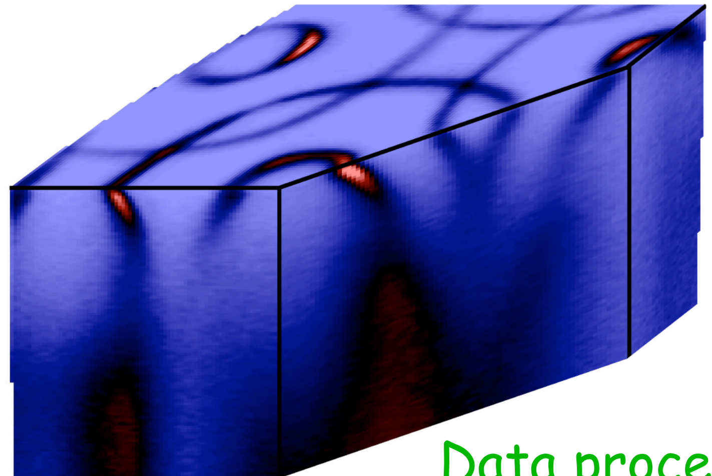
Angle-resolved Photoemission Spectroscopy



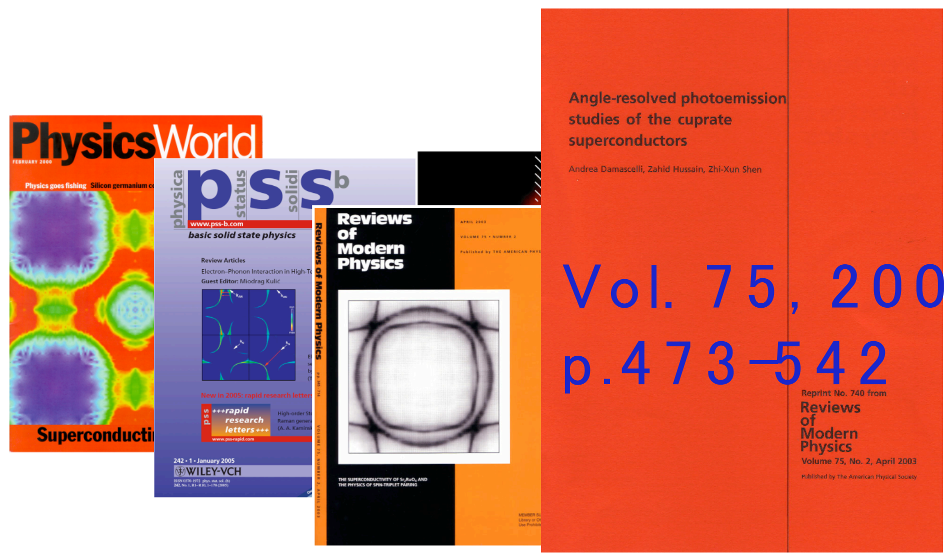
Instrumentation



Materials



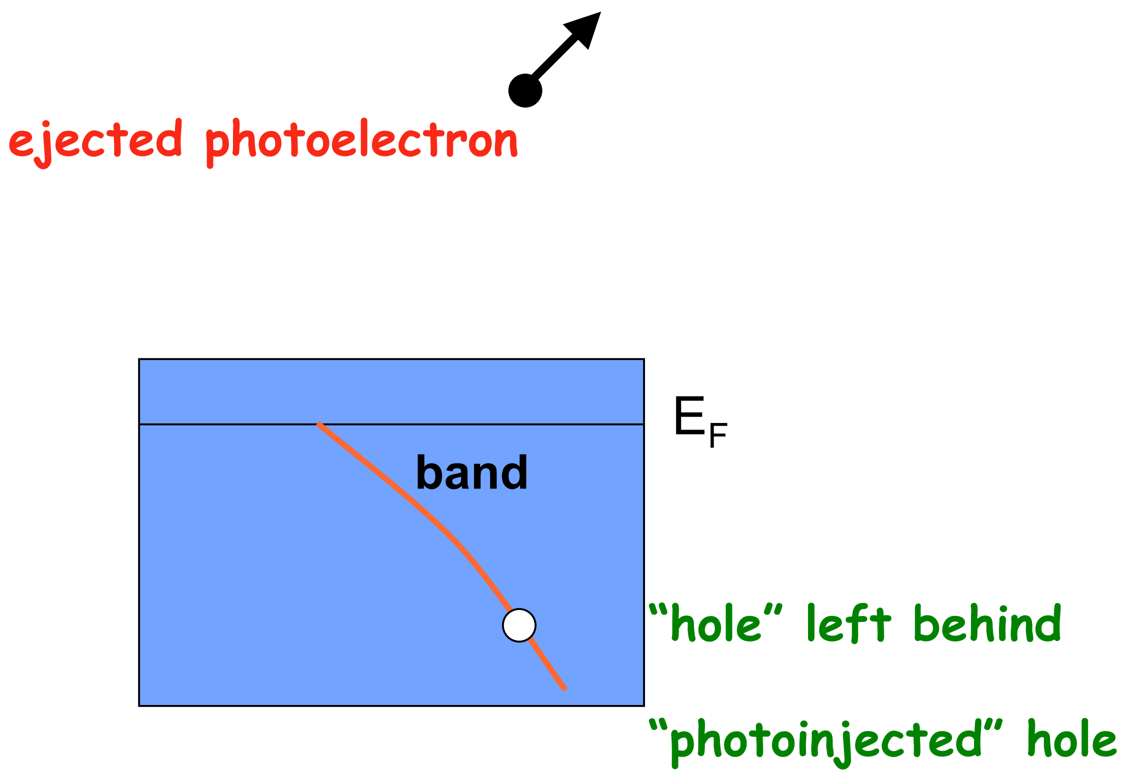
Data processing



Vol. 75, 2003
p.473-542

Scientific issues

What does ARPES measure?



Properties of the photoelectron reflect the properties of the injected hole

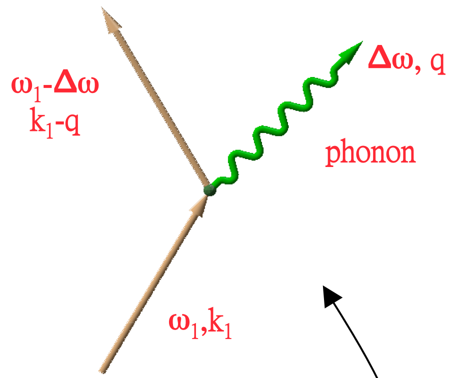
namely,

we can learn about the scattering and lifetime of the injected hole

Courtesy: Eli Rotenberg

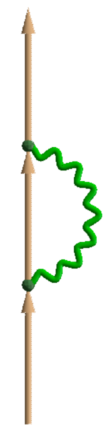
“kinkology”

The carriers have a finite lifetime due to absorption and emission of <u>phonons and other excitations</u>



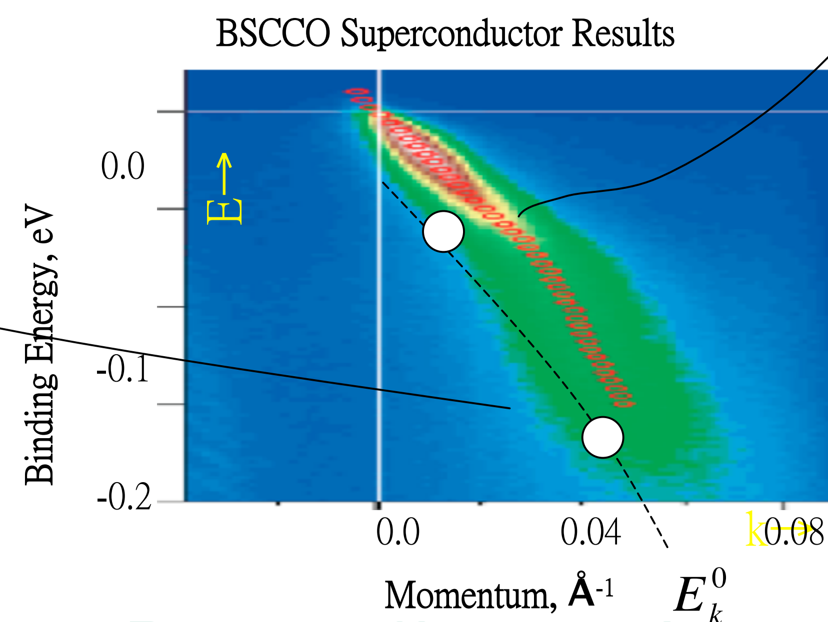
electron emits a phonon:
change of energy ω and momentum k

the measured state is broader in momentum and energy



electron emits and reabsorbs a phonon: change of mass

the mass of the carrier is increased



these processes are <u>fundamental</u> to understand superconductivity

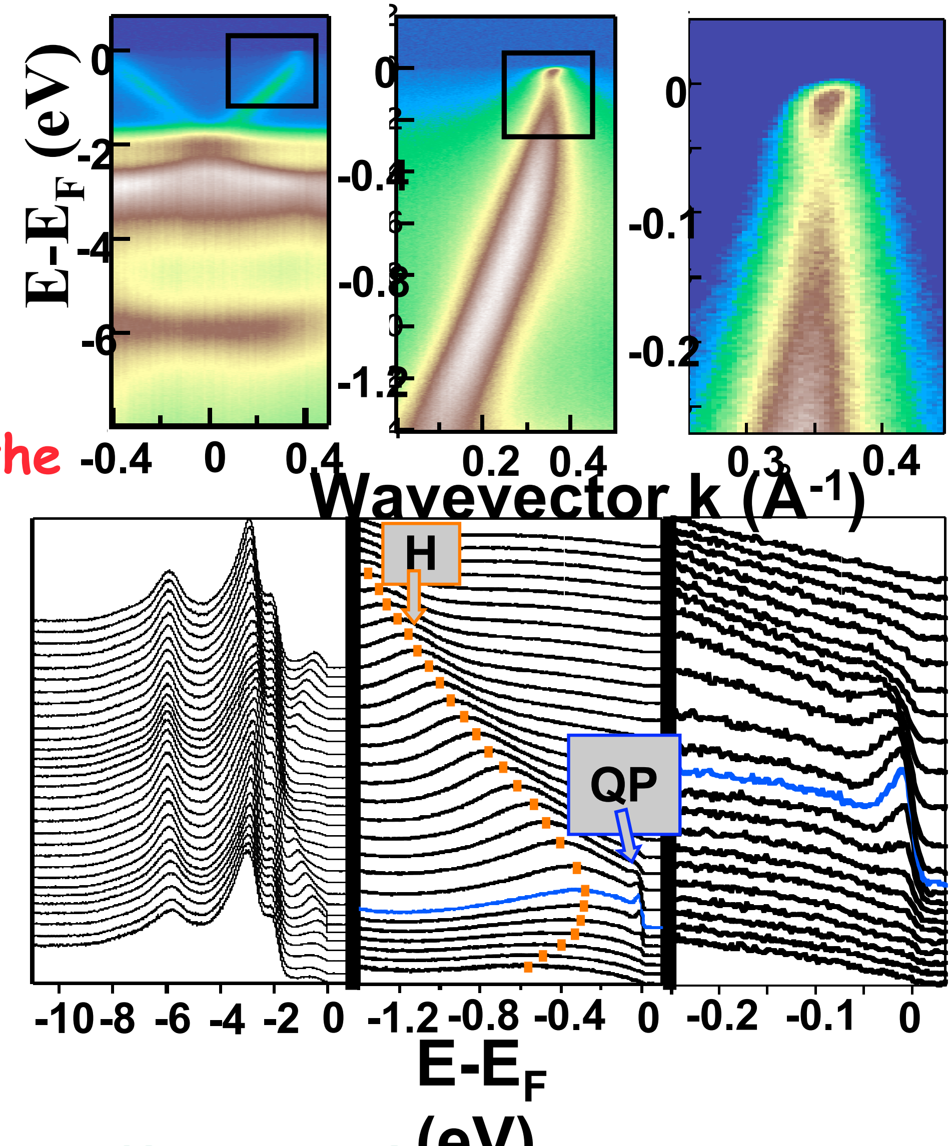
ARPES is the most developed technique to probe these processes measurments

Courtesy: Eli Rotenberg

[1] Koralek et al, Phys. Rev. Lett. 96, 017005 (2006)

Quasiparticle in Manganite: LSMO x=0.4

- Nodal quasiparticle:
- nodal-antinodal dichotomy in a *non* superconducting material
- Are the pseudogap state & the nodal-antinodal dichotomy hallmark of the superconductivity state?

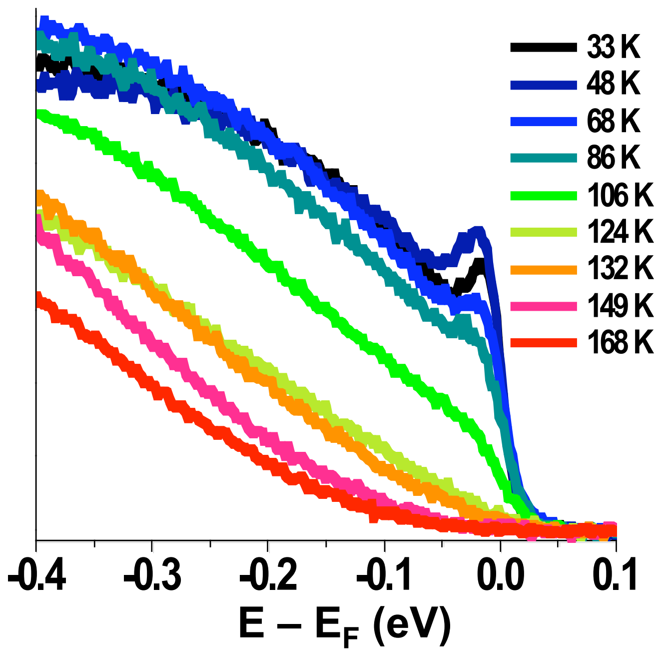


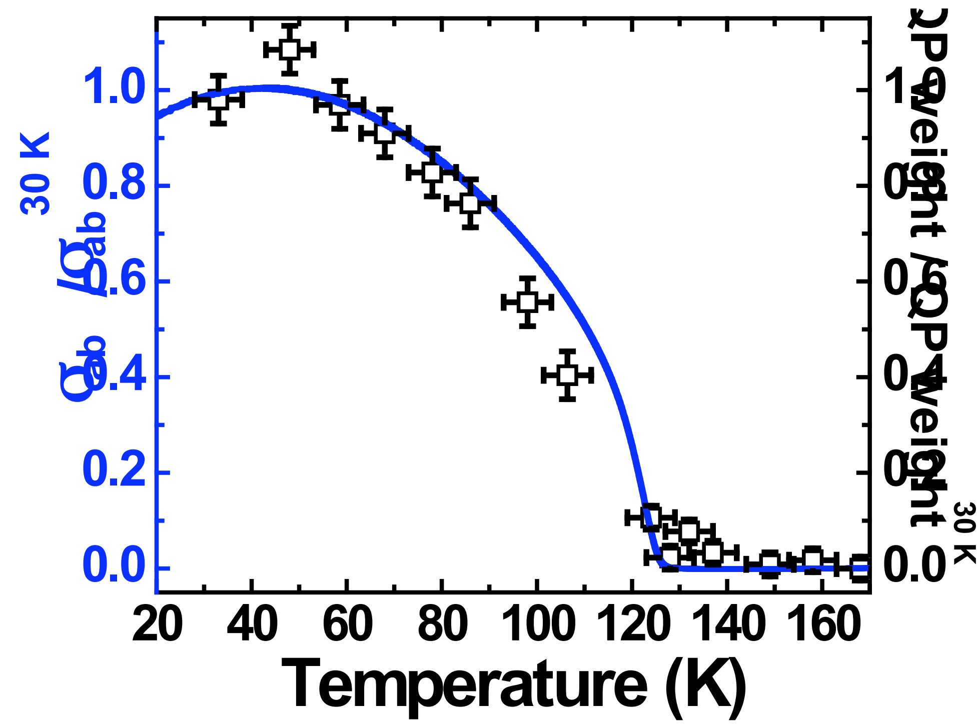
N. Mannella et al.
Nature 438, 474 (2005)

Temperature evolution of the small QP peak linked to transport properties

and the metal-insulator transition in LSMO

Mannella et al

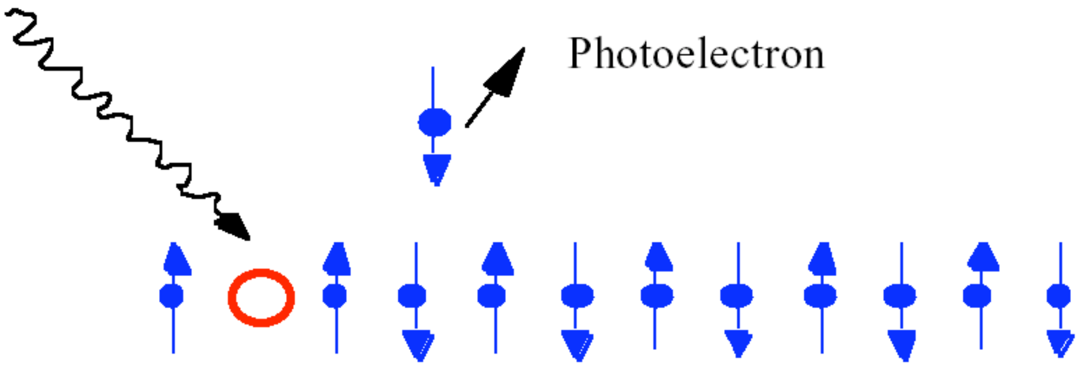


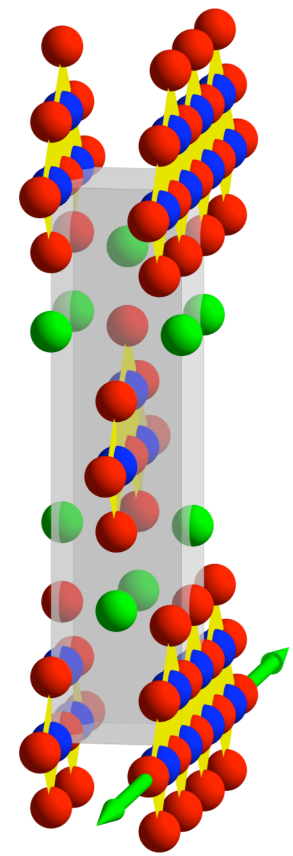


How could measurement of a microscopic electronic structure in certain part of the BZ could be related to the bulk macroscopic property?

Spin-Charge Separation

1D SrCuO2





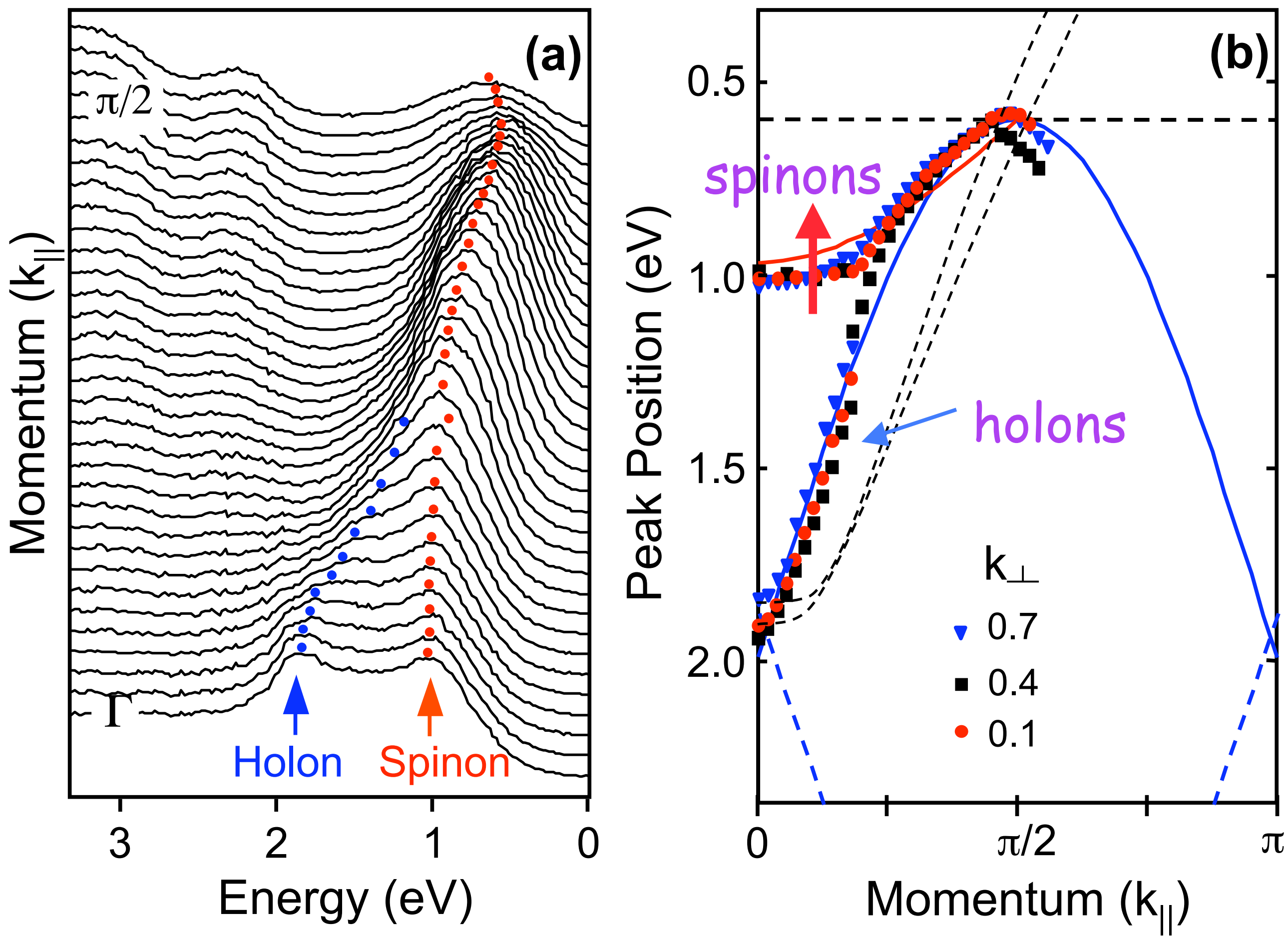
Photohole decay into

Two topological defects

Spinon: speed controlled by J (exchange Coupling constant)

holon: speed controlled by t (nearest-neighbor hopping Amplitude)

Spin-Charge Separation in 1D $SrCuO_2$

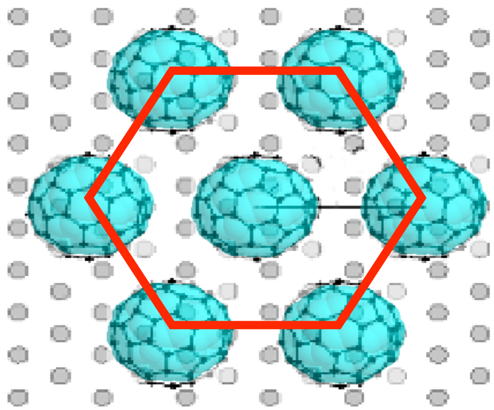


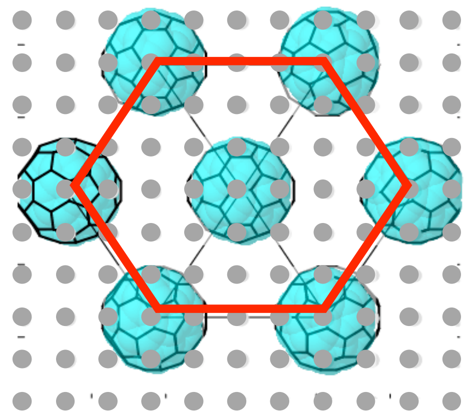
Holons and spinons have different mass & thus different dispersion (Fermi velocity).

B.J. Kim, E. Rotenberg' C. Kim et al.
Nature Physics 2, 355(2006)

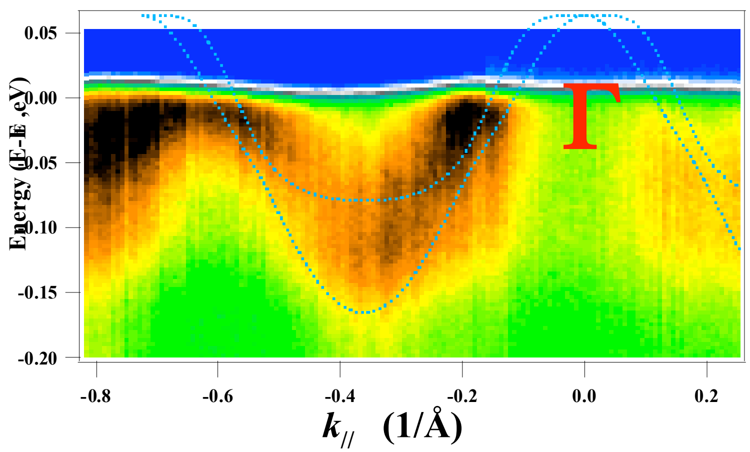
Band Structure of C_{60} on Ag (111) and Ag (100) Surfaces – Orientation Dependence

(111) surface

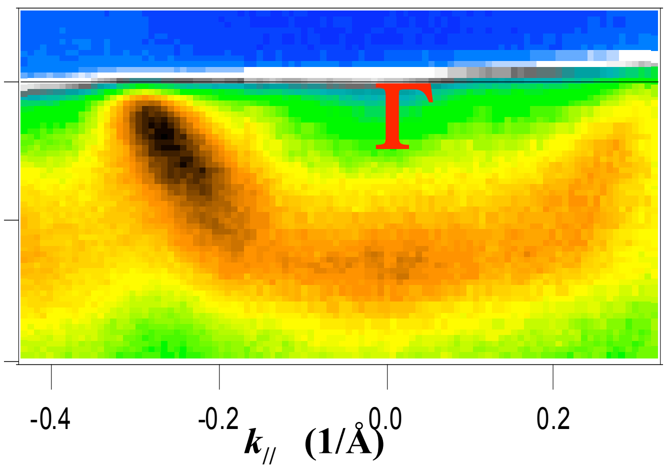




(100) surface



C_{60} ML / (111) surface

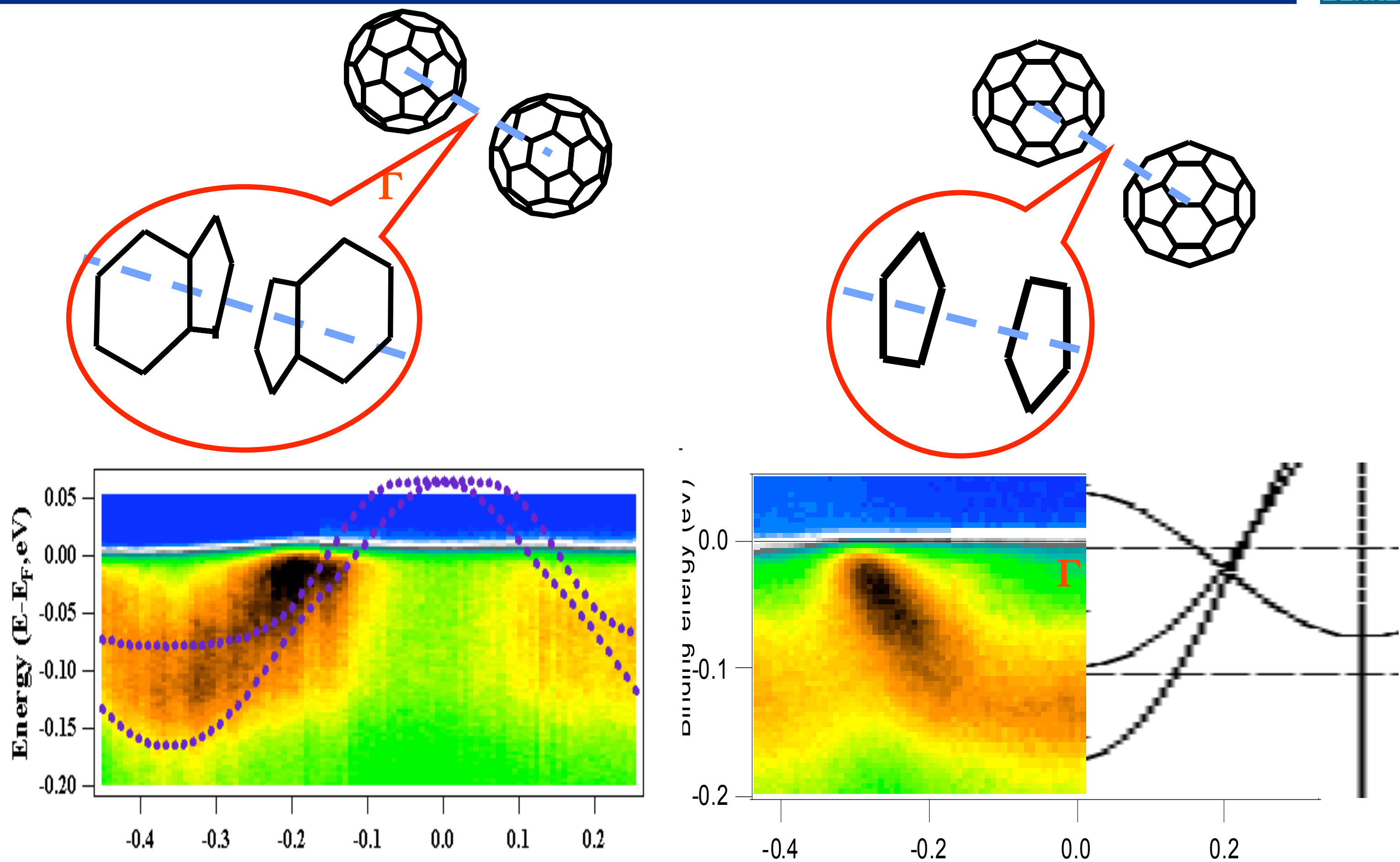


C_{60} ML / (100) surface

Same Hexagon Structure; Completely Different Dispersion!

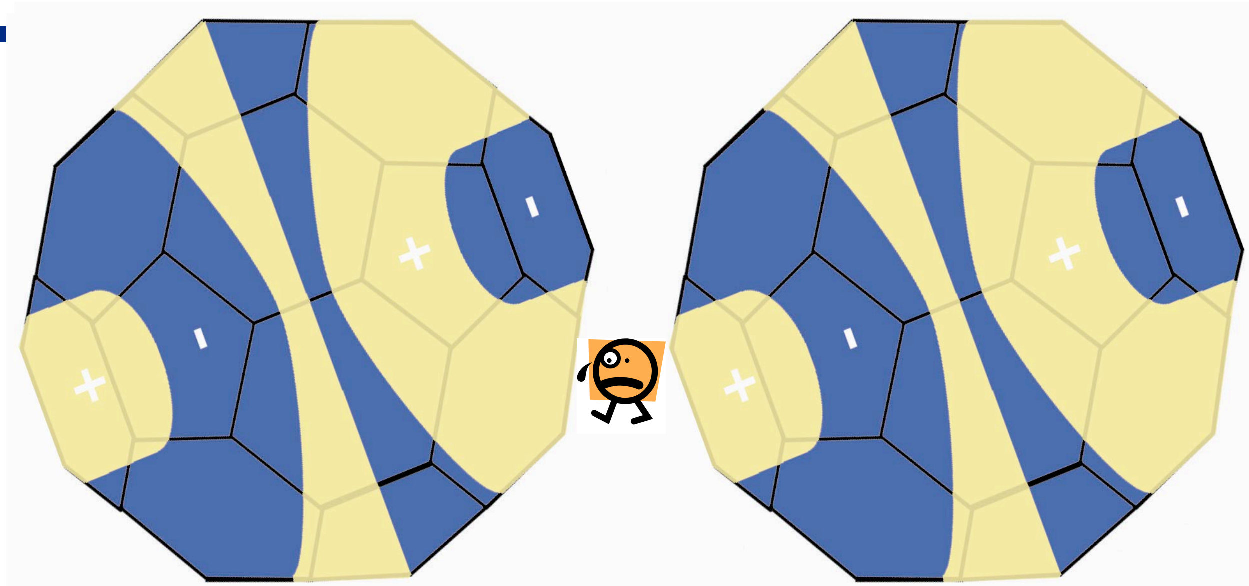
Brouet, Yang, Hussain, Shen et al, Science, 300, 303 (2003); PRL (2004)

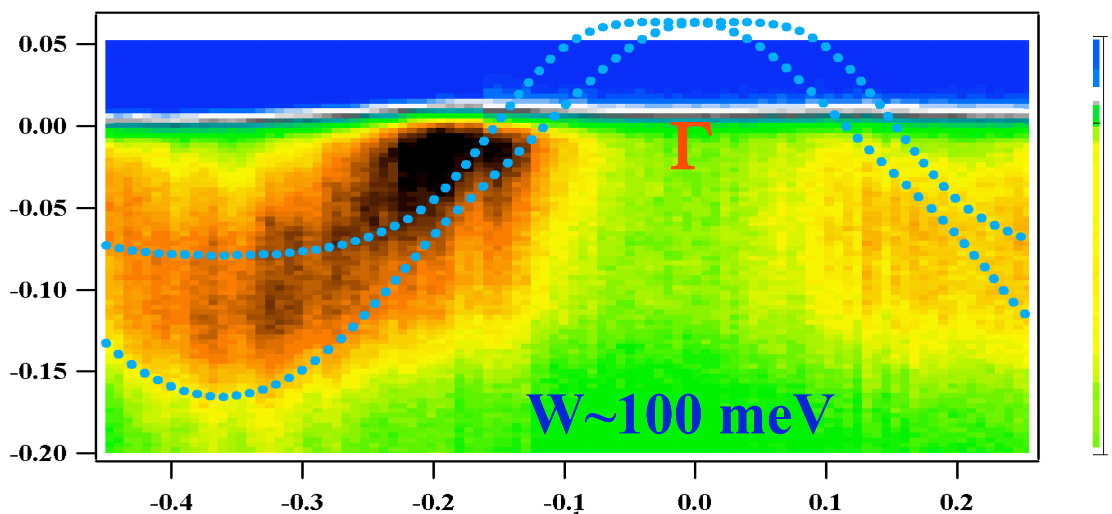
Combination of Experiment and Theory (strong orientation dependence)



Dotted Lines: Theory (Louie, Cohen et al) LDA);
2D Images: Experiments

C60 (Conclusion)





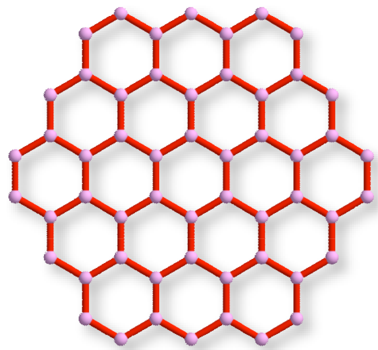
Wang, Brouet, Louie, Hussain, Shen et al

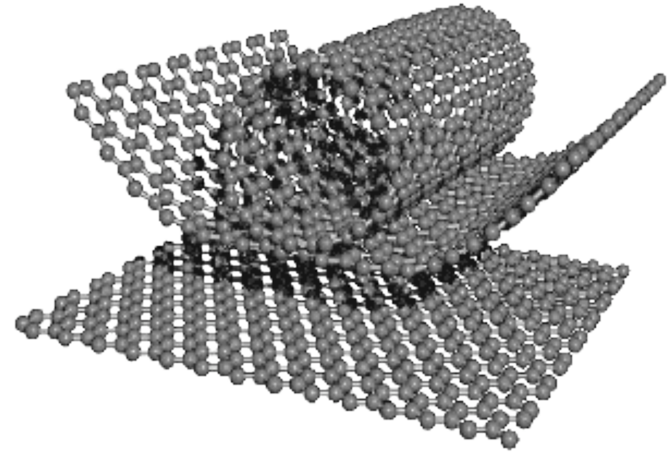
Science <u>300</u>, 303(2003)

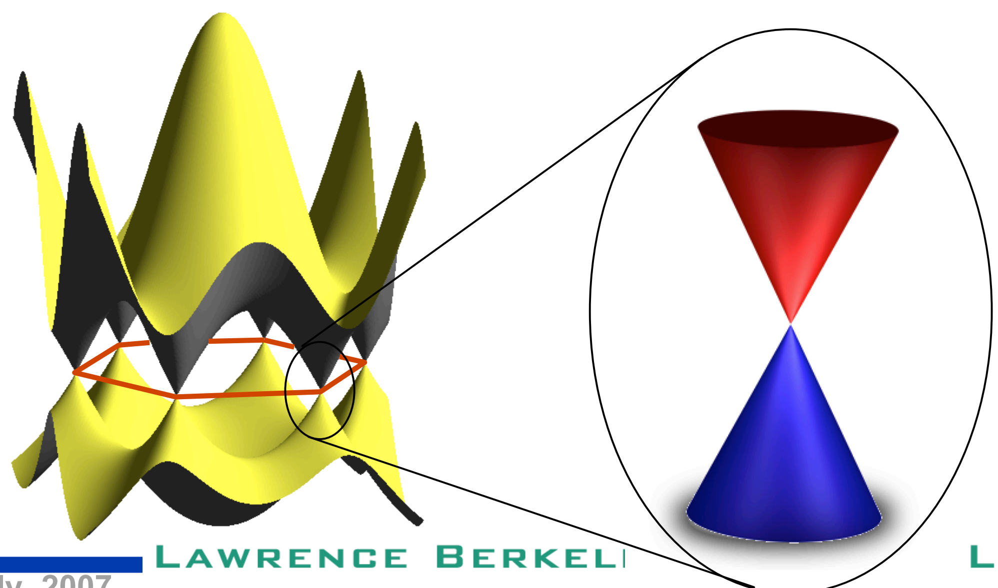
PRL<u>93</u>, (2004)

Purely Two Dimensional State: Graphene

Graphene: A single hexagonal sheet
of Carbon atoms that is the building block
of carbon nanotubes, graphite, buckyballs, and
other C-based materials







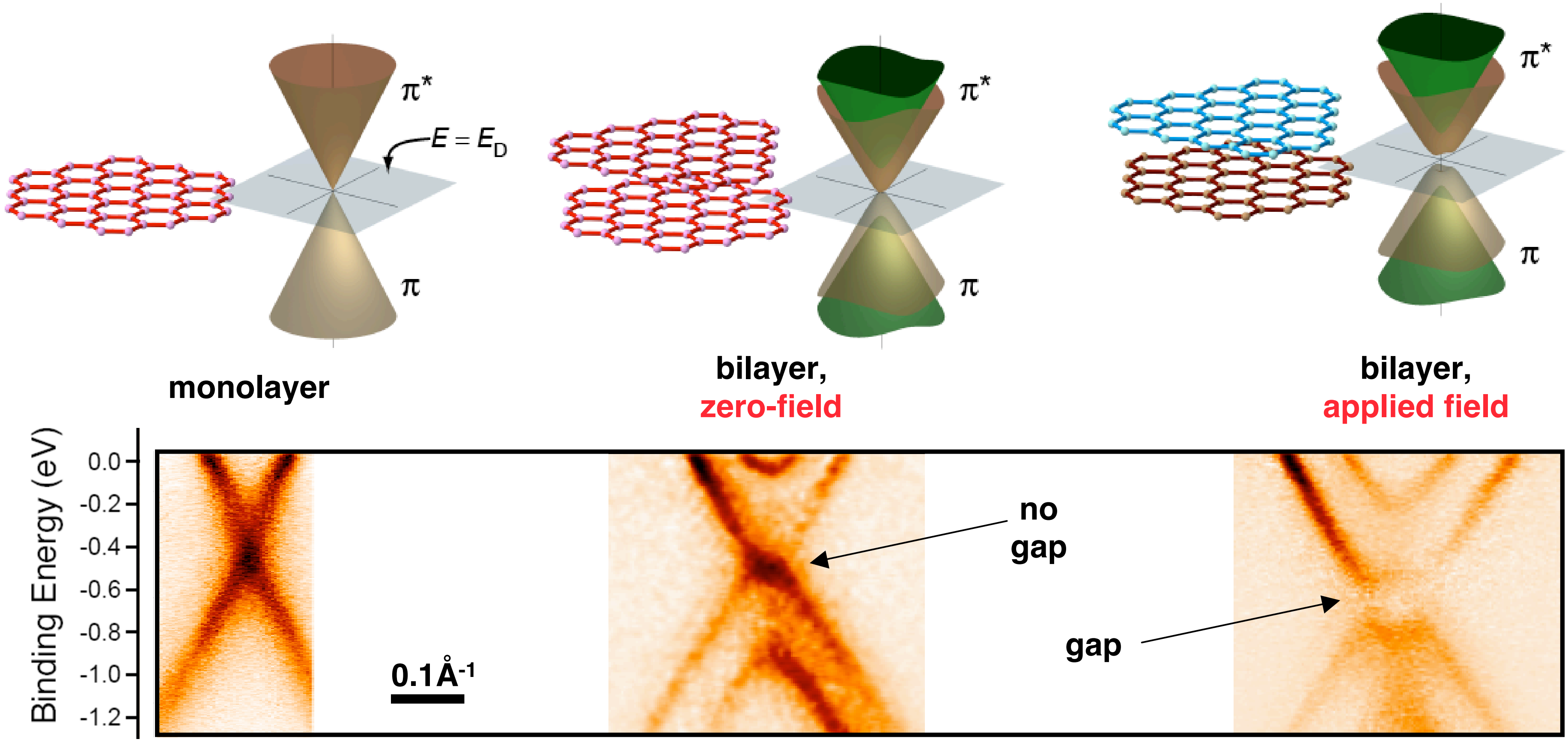
A gapless semiconductor with a famous conical bandstructure.

- ballistic transport at room temperature
- high current capacity (130 nA per nanotube, or 100,000,000 A/cm^2

By imposing a gate voltage on a graphene layer we can easily tune the doping from *n* to *p* type, and we can realize a new generation of ultra-small, high current capacity devices.

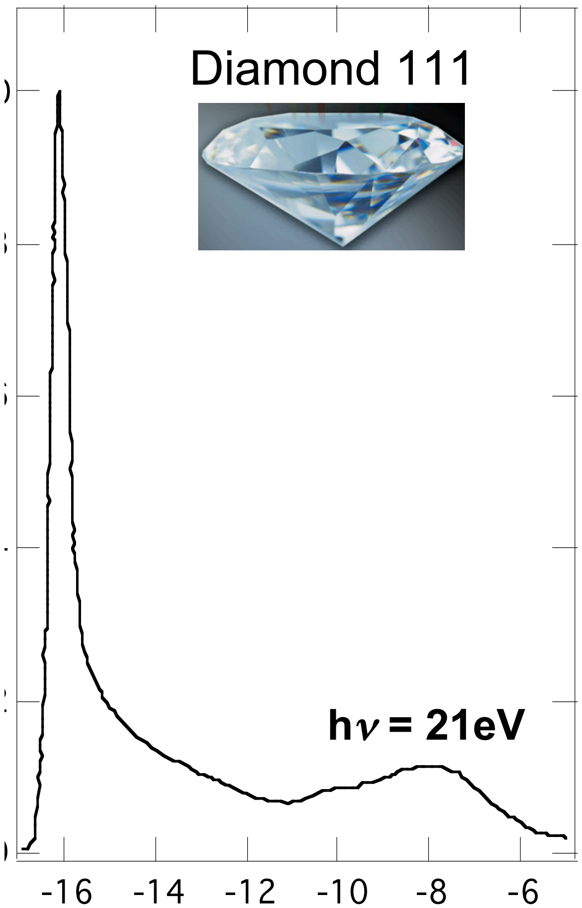
Example 2: Breaking down the barriers to carbon-based electronics

- The electronic properties of graphene depend on the thickness and applied field.
- Demonstrating the possibility of 0.6 nm thick switches based on carbon.

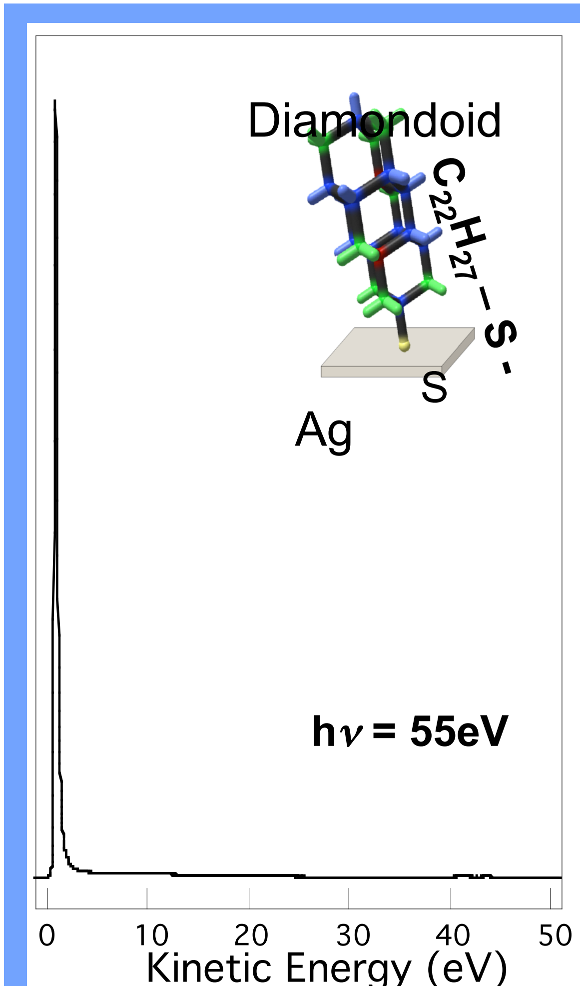


Ohta, T., Bostwick, B., Seyller, T., Horn, K. & Rotenberg, E.
Controlling the Electronic Structure of Bilayer Graphene. Science 313, 951-954 (2006).

Photoexcited Electron Emission from Diamond and Diamondoid-thiol Self-assembled Monolayer



Himpsel etc. 1979 (Wisconsin)
Pate etc. 1986 (SSRL)

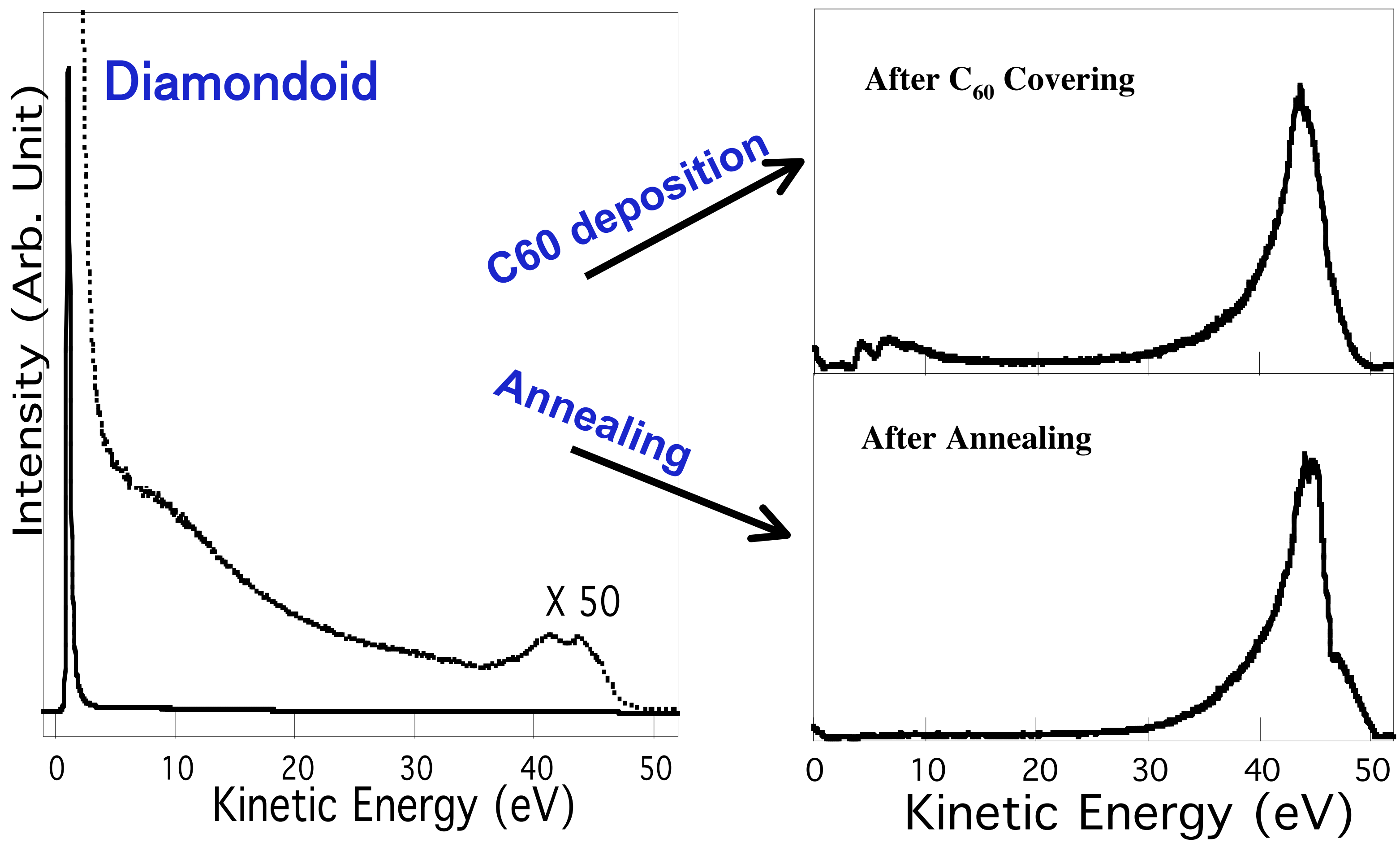


Tetramantanethiol (4-cage)

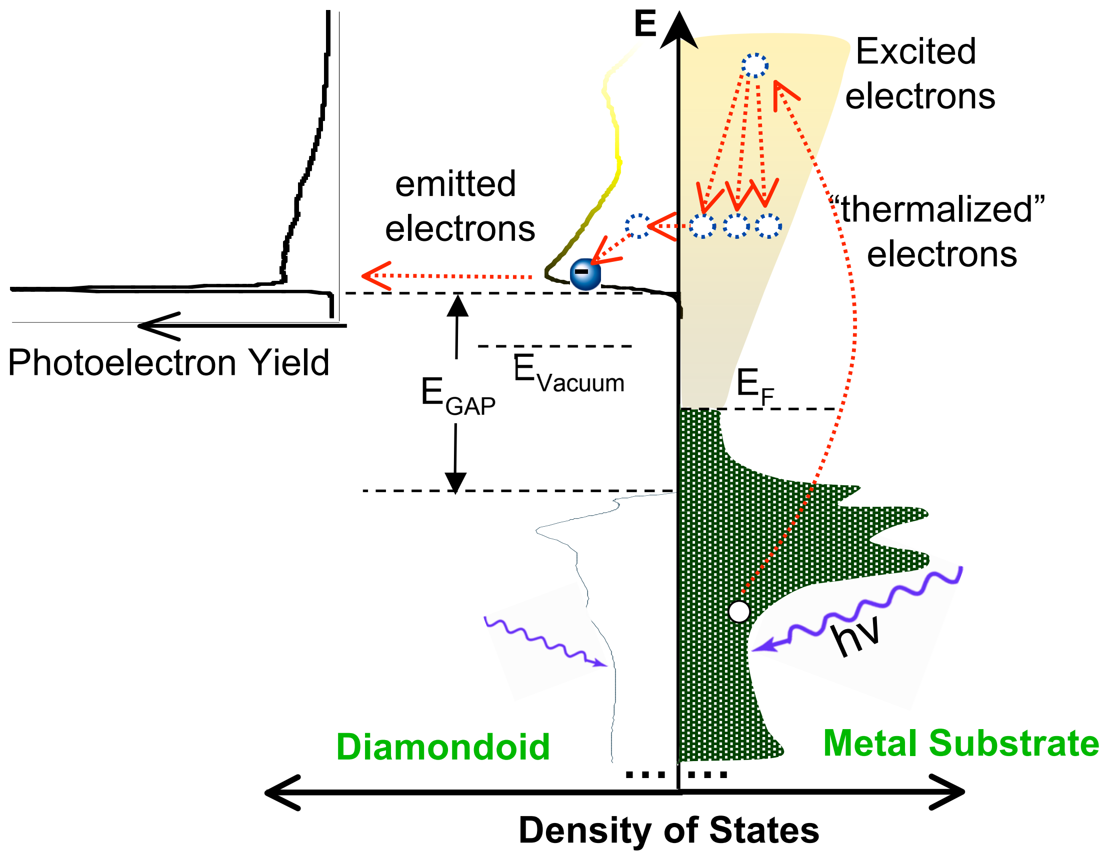
- **Self Assemble on Metal Surface (Ag, Au, …)**
- **Natural resource (oil field)**
- **More uniform**
- **5 times more effective**
- **Better electron conductivity**

WL Yang, Z Hussain, ZX Shen, *Science* 2007 (ALS)
Patent filed, Stanford-LBNL-Chevron

Surface Destruction Test

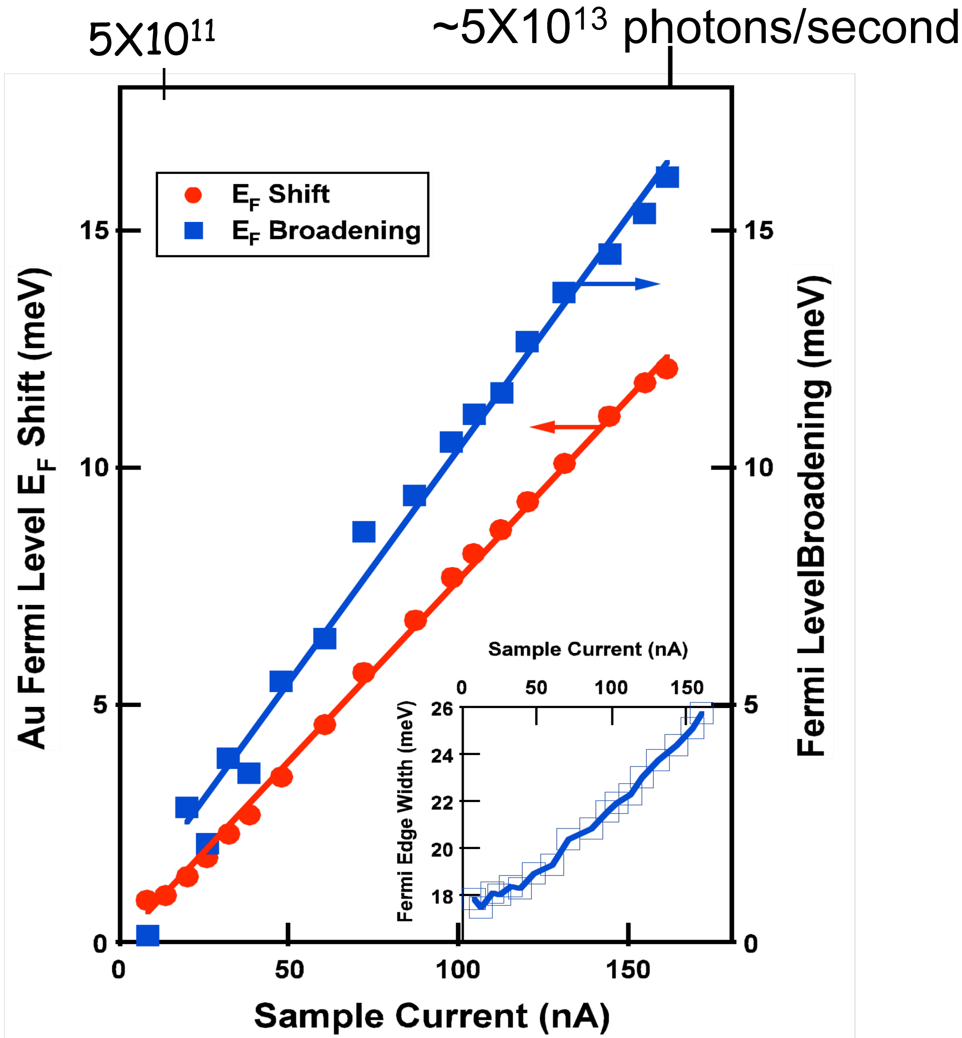


Electron Emission from Diamondoid



Space Charge Effect in Photoemission

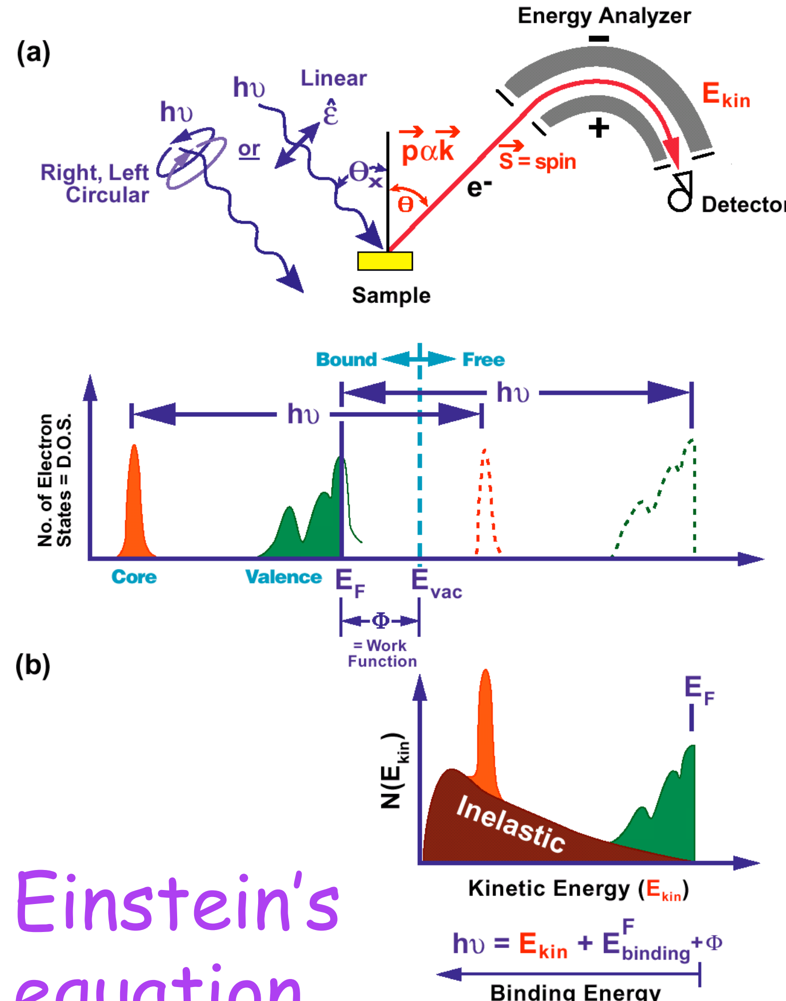
Caution



X. J. Zhou, B. Wannberg, W. L. Yang, V. Brouet, Z. Sun, J. F. Douglas, D. Dessau, Z. Hussain, Z.-X. Shen, J. Electron Spectroscopy and Related Phenomena, 142, 25 (2005).

What are new opportunities with core level photoemission ?

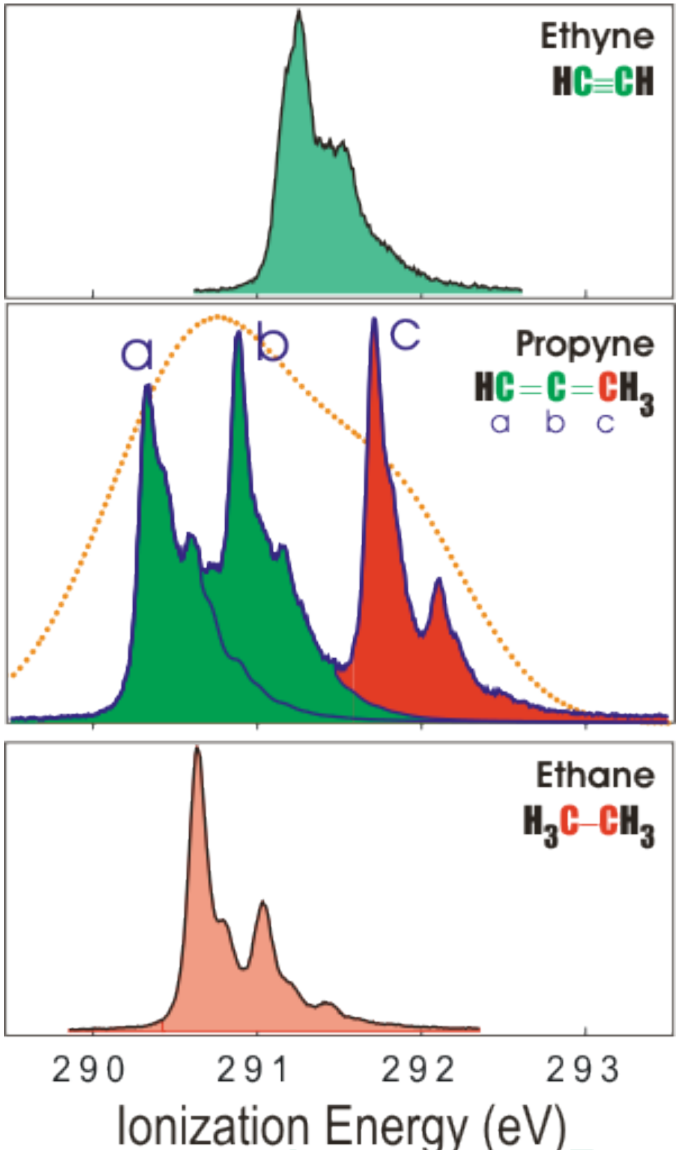
In-Situ & _dynamical_ studies of chemical reactions at surfaces



Einstein's equation

ag.zh/photospectros1/7-97

High resolution C1s Photoelectron Spectra of hydrocarbons (sharper tool with modern SR)



C 1s photoelectron spectra of propyne (res: SR~30meV, lab source ~ 0.5 eV (dashed))

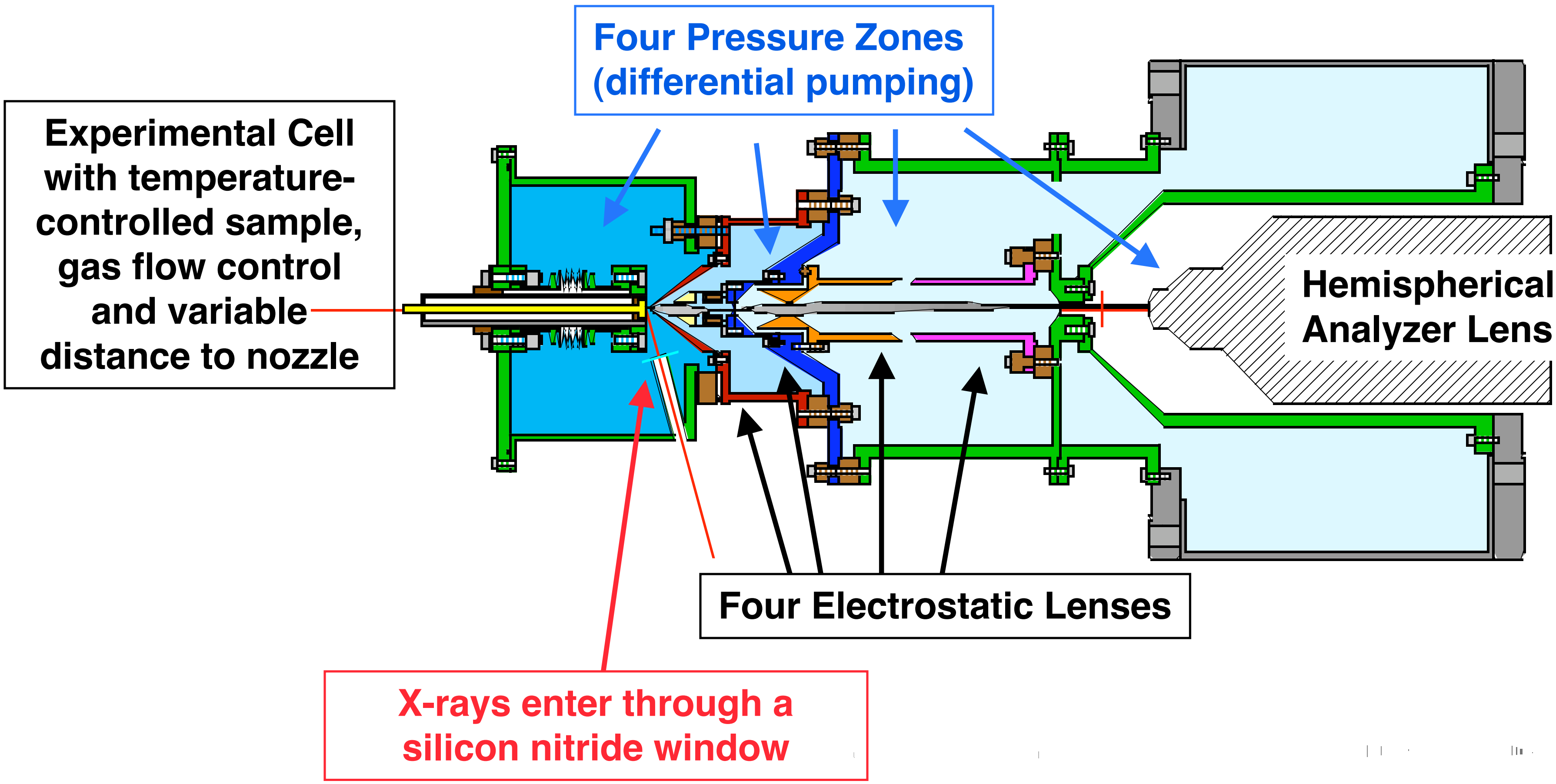
Unambiguous assignment of peaks in propyne spectrum is made possible by characteristic vibrational structure of model compounds (ethyne and ethane)and abinitio theory.

Shift of the methyl (CH3) peak in propyne relative to ethane is due to the electronegativity of the ethyne (HC°C) group.

From BL 10.0 (AMO, ALS)
Thomas et al, PRL

Ambient pressure photoemission

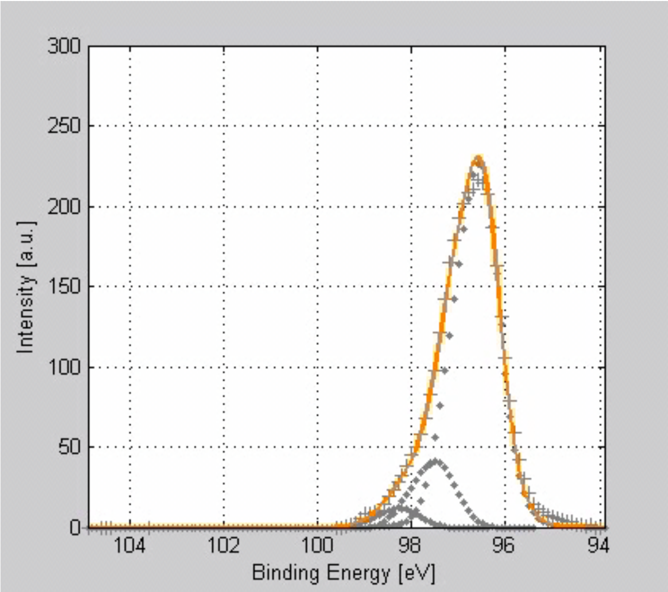
Ambient Pressure Photoemission: ~ 10 torr

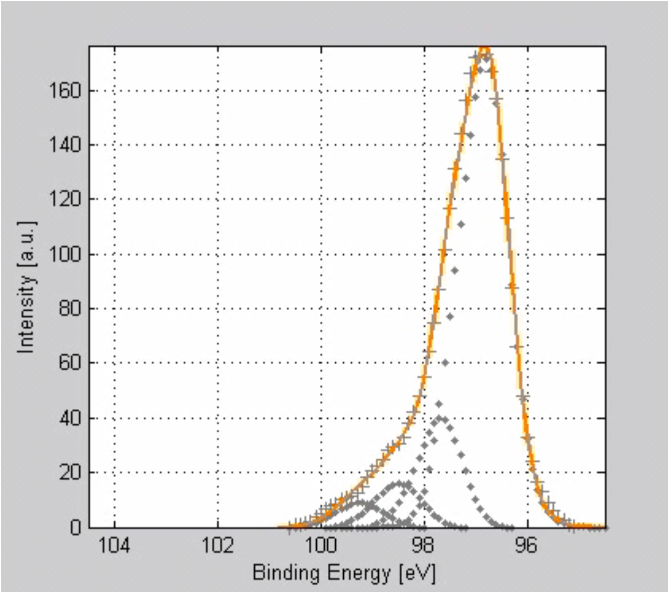


D.F. Ogletree, H. Bluhm, Ch. Fadley, Z. Hussain, M. Salmeron, Materials Sciences Division and Advanced Light Source, LBNL.

Oxidation dynamics

Strong temperature dependence





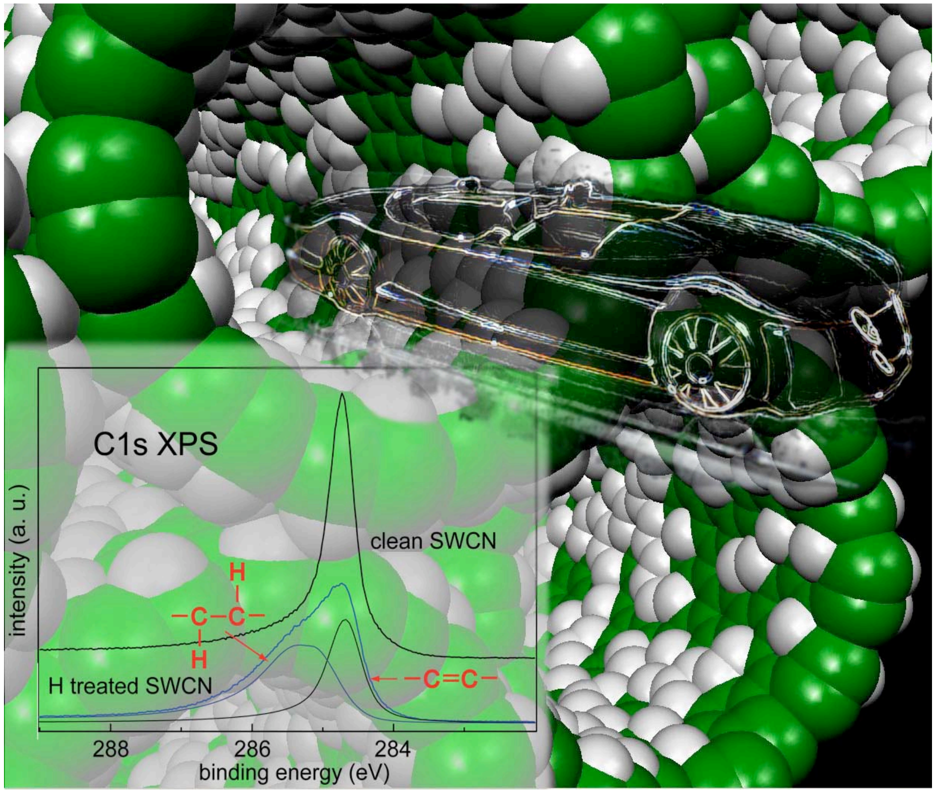
250°C — Si^{4+} — Si^{+0} Bulk

450°C — Si^{4+} — Si^{+0} Bulk

Si(100) oxidized by water vapour @ .1 torr

(S. Mun et al)

Steps Toward Hydrogen Vehicles



Nikitin et. al., *Phys Rev Lett.* **95**, 225507 (2005)

Characterising new materials:

Carbon Nanotubes for storing hydrogen: safely, efficiently and compactly.

The DOE Freedom CAR program has set the goal of a material that can hold 6% of the total weight in hydrogen by the year 2010. Theoretical calculations indicate they may exceed these goals substantially.

Funded by DOE, NSF and Global Climate and Energy Project (alliance of scientific researchers and leading companies in the private sector, including ExxonMobil, General Electric and Schlumberger)

The Ultimate Solution : Energy Problem (Hope!)

- Need study of transition metal oxides as Photocatalysts for breaking the water using sun light (tailor properties using emergent phenomena and quantum confinement.

"Honda-Fujishima Effect"

- TiO_2 as a Energy Source

  Hydrogen Production from the Water $(H_2O + \text{photons} \rightarrow H_2 + \frac{1}{2}O_2)$

  (problem: only absorbs UV light, look for other catalyst)

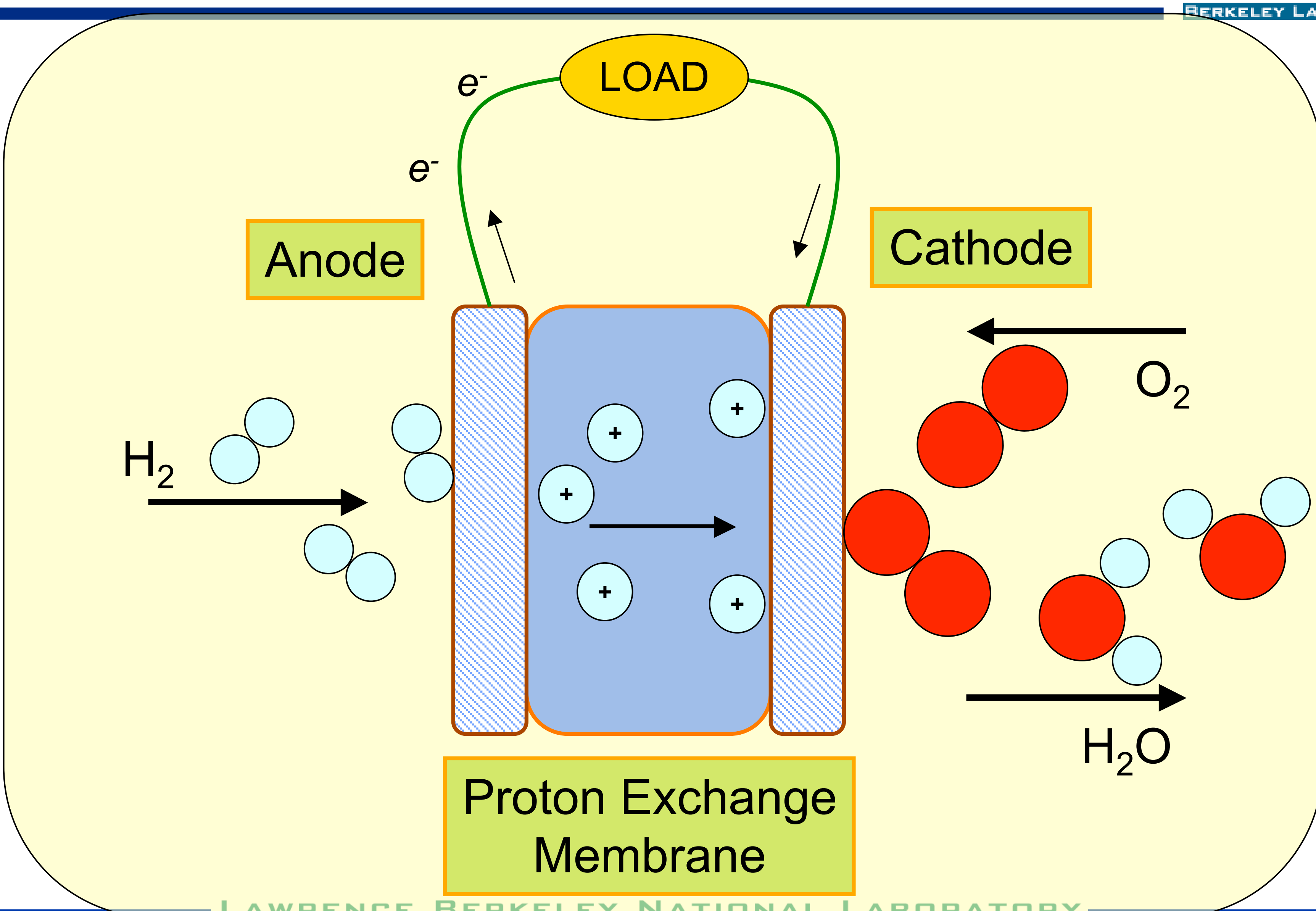
- **High payback!**

  - Unlimited source (water + solar light)
  - Very Clean and Recyclable Exhausts $(H_2 + \frac{1}{2}O_2 \rightarrow H_2O)$

  (Fuel Cell)

courtesy:Akira

Fuel Cell - Schematic



Anode : Hydrogen oxidation

Hydrogen gas = Hydrogen Ions + Electrons

$$2H_2 \rightarrow 4H^+ + 4e^-$$

Not too weak!
Not too strong!

Conducting through Membrane

External Circuit

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

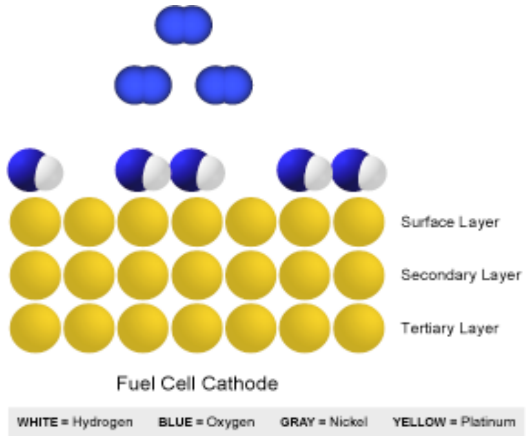
Cathode : Oxygen reduction

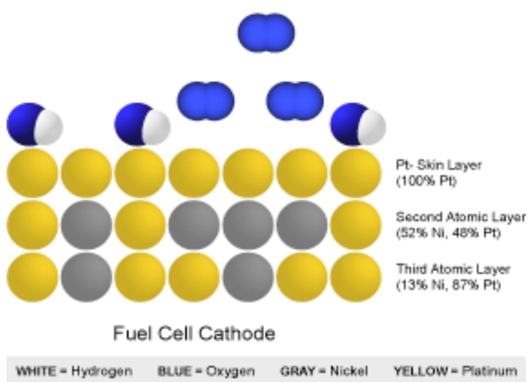
Oxygen gas + Protons + Electrons = Water

In both cathode and anode, Pt based catalysts are applied to increase the rate of each chemical reactions. Need better material than presently used Pt.

Cathode : the performance of polymer electrolyte membrane fuel cells is limited by the slow rate of O_2 reduction (ORR) at Cathode, ~5 orders of magnitude slower than H_2 oxidation at Anode

Breakthrough Research For Fuel Cells





Hydrogen powered fuel cells for automotives are one of the cleanest and most efficient technologies for generating electricity. But until now, progress is slow.

The discovery of a unique ***platinum-nickel alloy*** represents a breakthrough in catalyst research: **it is *90 times more active* than state-of-the-art platinum catalysts currently used.**

Science 315 Jan 2007

Research team includes: Argonne and Berkeley National Labs, U. South Carolina.

In standard Pt catalysts (top) absorption of oxygen on the surface is hindered by the binding of other molecules, such as OH. In the new material (bottom) The nickel atoms change the surface properties such that OH cannot bind as well, leaving room for oxygen.

Scientific opportunities with ARPES

for unraveling of complex problems

X-ray Spectroscopy of Condensed Matter

Quantum Number Selectivity:

✓ Absorption

$$\omega\ \varepsilon_2 \Rightarrow \Delta E = E_f - E_\iota$$

✓ Angle-integrated photoemission

$$N(E,\hbar\omega) \Rightarrow E_f, E_\iota$$

✓ Angle-resolved photoemission (also inelastic scattering)

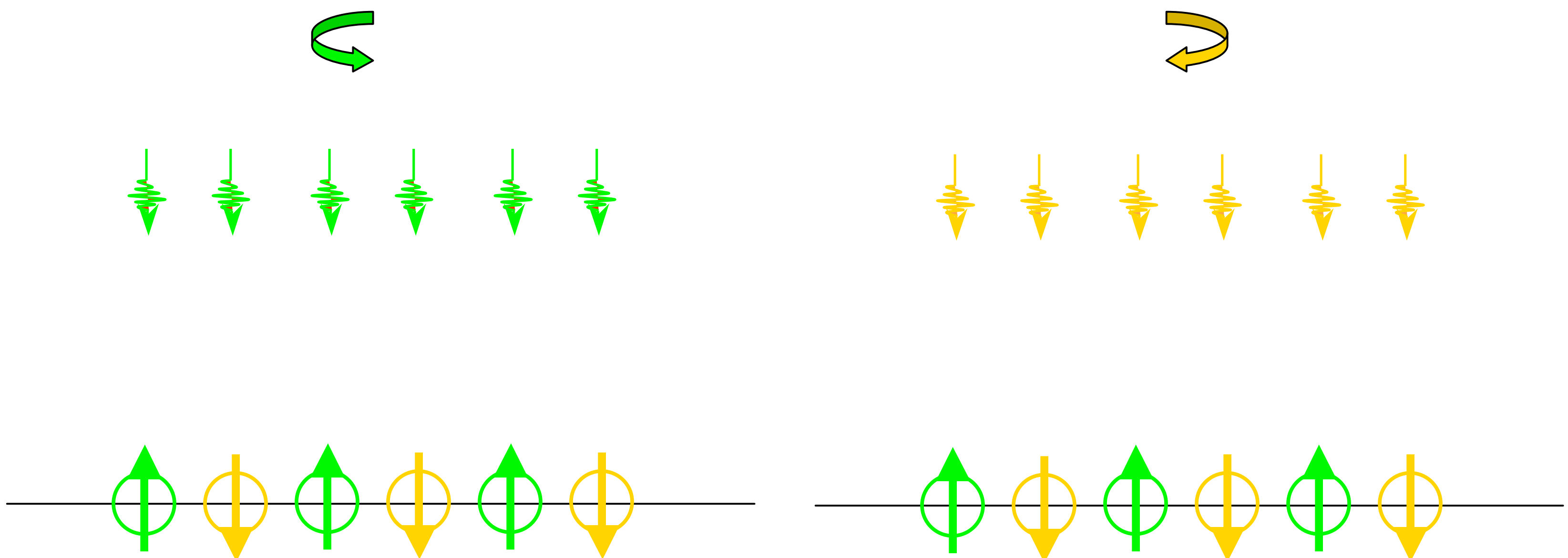
$$N(E,\hbar\omega,\theta,\varphi) \Rightarrow E_f, E_\iota; \vec{\kappa}$$

!!! Spin-polarized photoemission

$$(N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow) \Rightarrow E_f, E_\iota; \vec{\kappa}, \vec{\sigma}$$

Photoemission with circularly polarized light and spin detection

Selective excitations
(use of elliptically polarizing undulator)



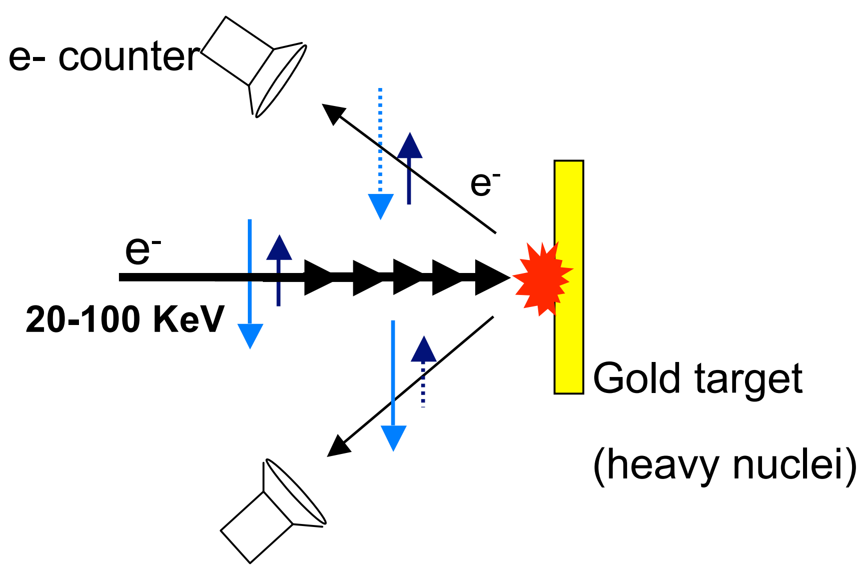
Courtesy: Yulin Chen

Spin detection (two schemes)

Mott Detector

Spin-orbit interaction

Hint = L · S



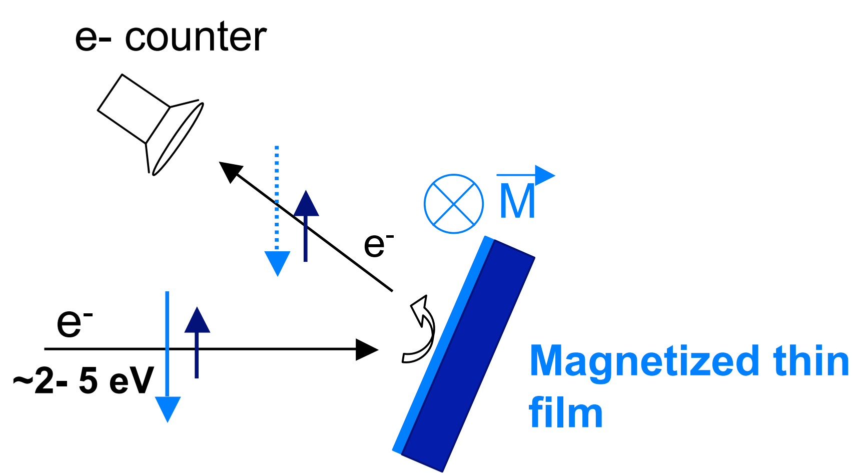
FOM ≤ 10^{-4}

D.T. Pierce et al. 1988 +….

Exchange scattering interaction

Reflectivity contains a term:

α P · M



x 100

FOM ~ 10^{-2}

R. Bertacco et al. 2001
Hillebrecht et al. 2002
R. Zdyb and E. Bauer 2003

Spin-Resolved Photoemission (TOF Project)

"Time-of-Flight" energy analysis

Multichannel detection in time (energy):

~ 10-100 times more efficient than single channel dispersive analyzer

"Exchange Scattering" based spin analysis

~ 100 times more efficient than Mott Detector

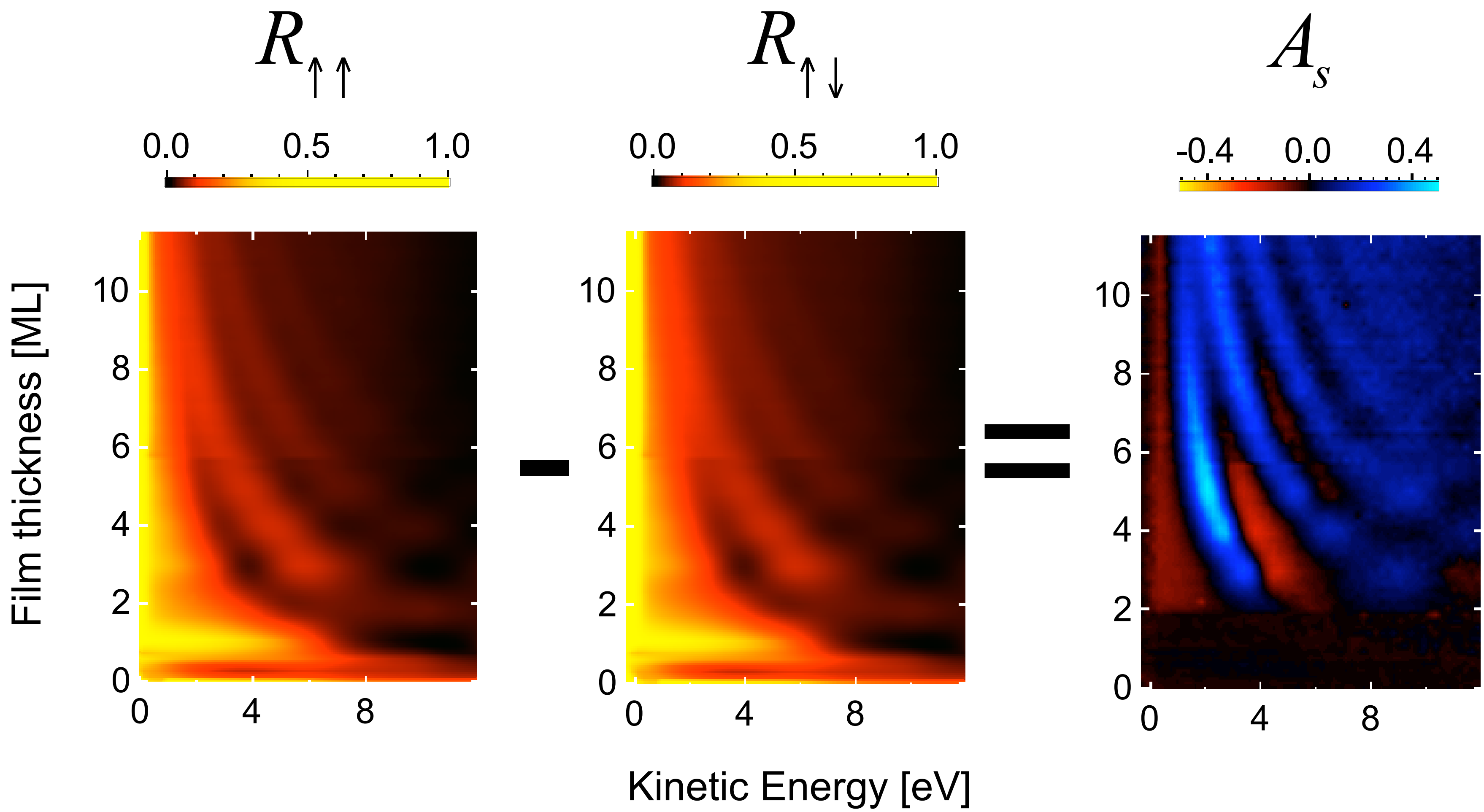
- Spin-Resolved ARPES: Improved efficiency & high resolution
  - Overall FOM: ~ 1000 times vs. existing (Mott det.+ dispersive analyzer)

energy resolution : ~ 10meV
Better statistics : > factor of 10

Note: TOF is inherently low noise detection as detector counts for short time; only the time window when electrons of interest arrive

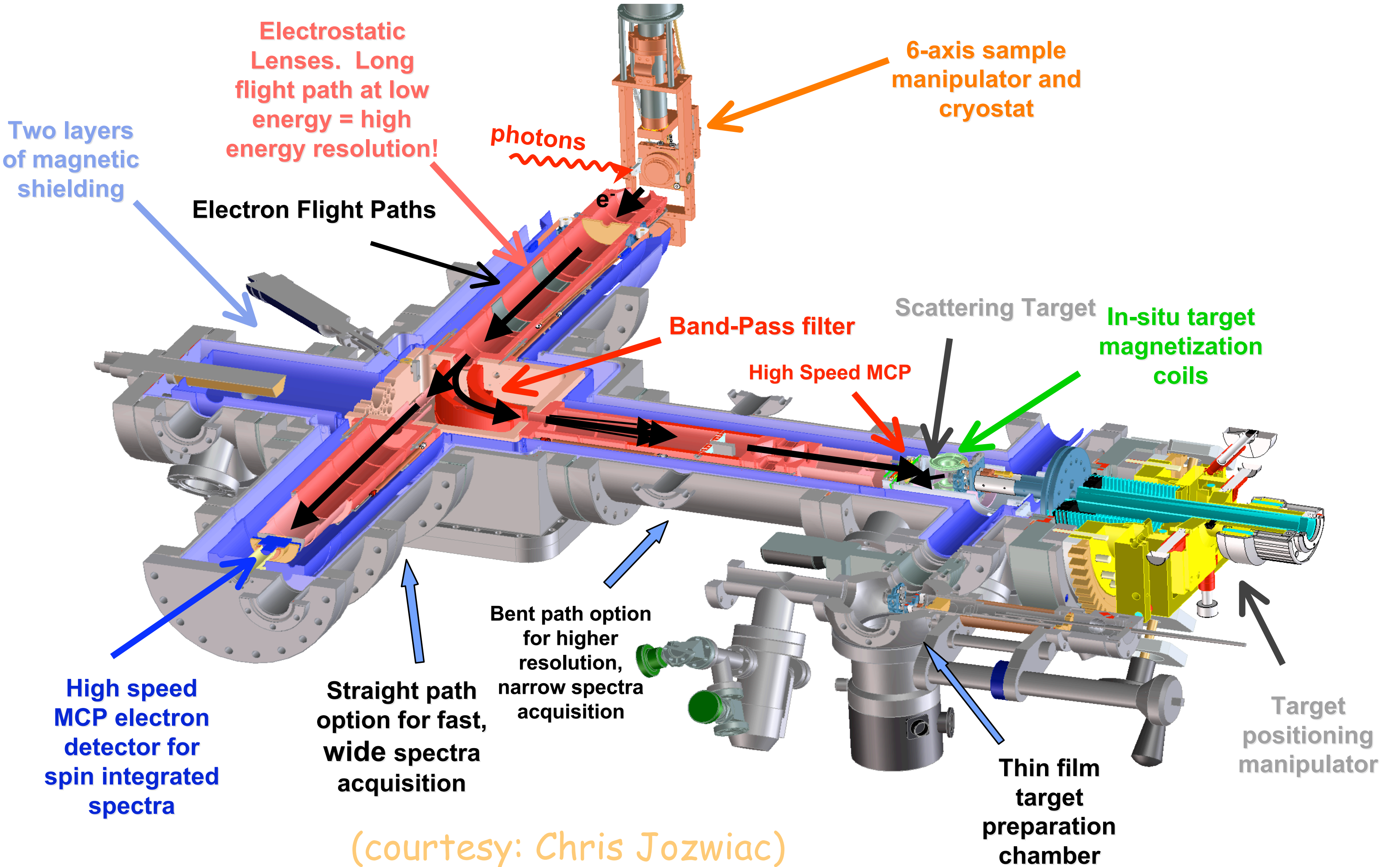
Graf, Schmid, Jozwiak, Hussain, Lanzara et al, PRB, 71, 144429 (2005)

Spin asymmetry (A_s): Co/W(110)
Experimental results using SPLEEM

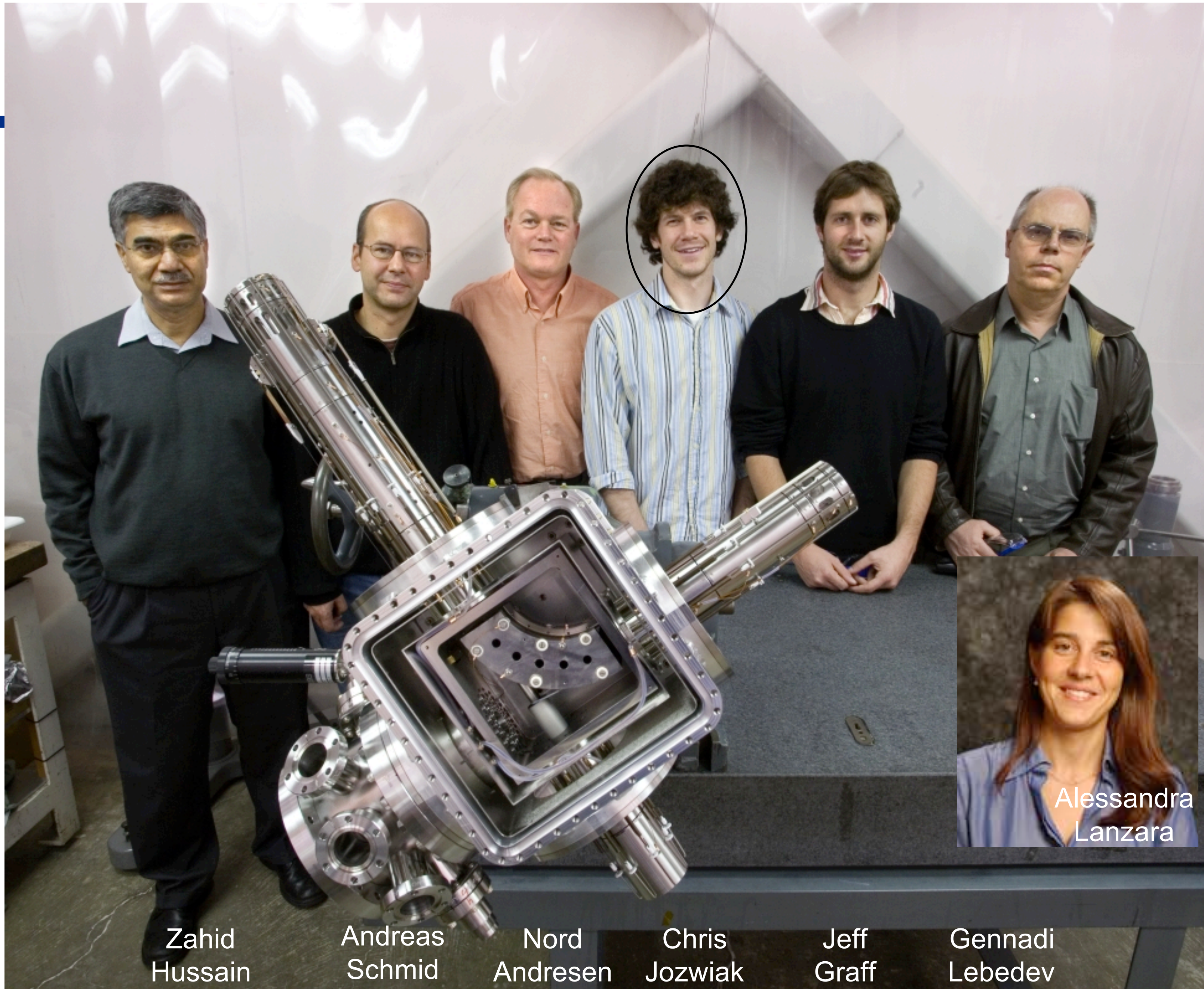


Graf, Schmid, Jozwiak, Lanzara, Hussain et al, PRB, 71, 144429 (2005)

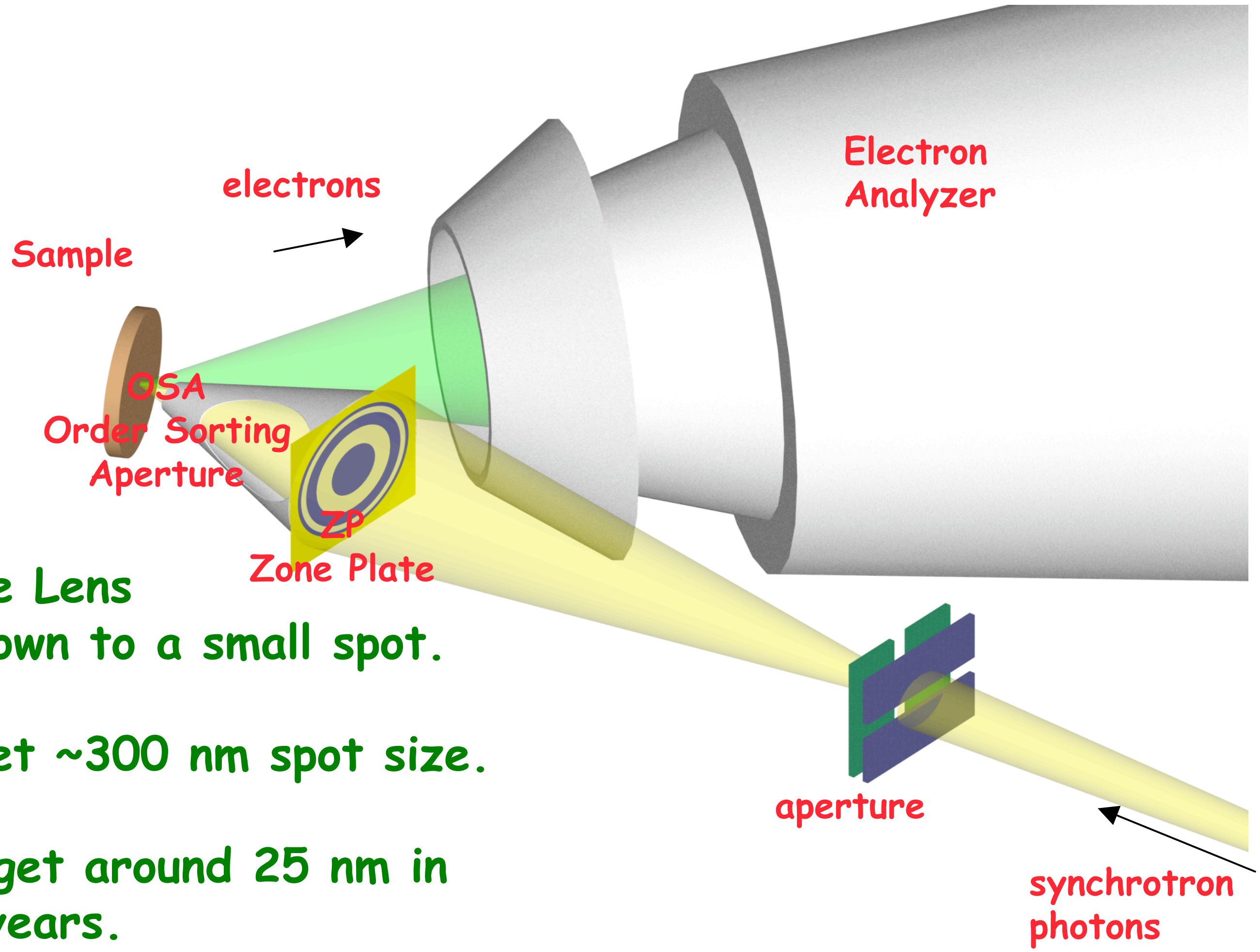
TOF Spin-Resolved Photoemission



(courtesy: Chris Jozwiac)


Zahid Hussain
Andreas Schmid
Nord Andresen
Chris Jozwiak
Jeff Graff
Gennadi Lebedev
Alessandra Lanzara

Nano ARPES



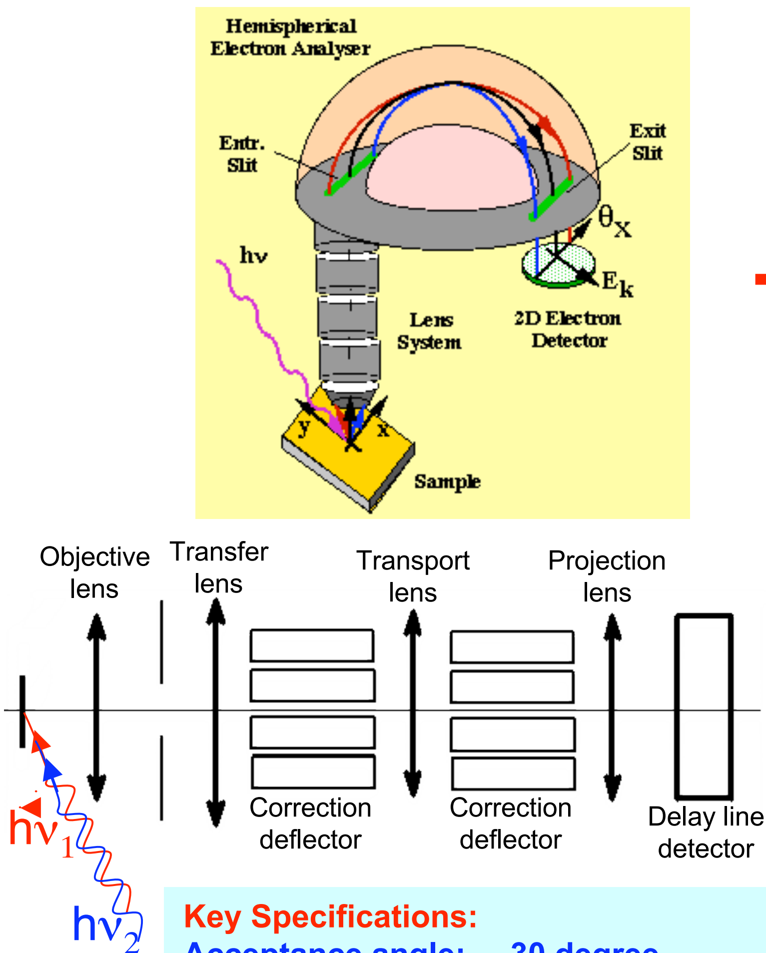
We use a Zone Plate Lens
to focus the light down to a small spot.

Currently, we can get ~300 nm spot size.

We are planning to get around 25 nm in
the next couple of years.

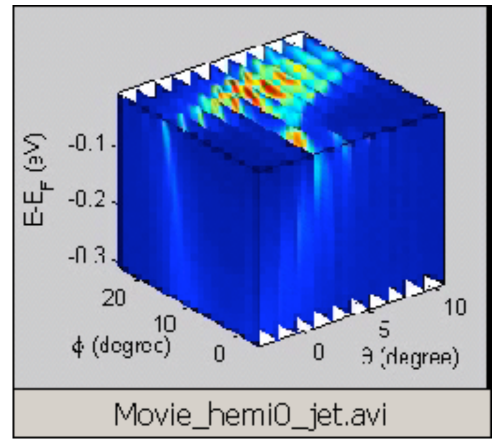
(lectured by Janos Kirz)

Time-Resolved Photoemission
Comparison of the Hemispherical Analyzer and the TOF Analyzer proposed



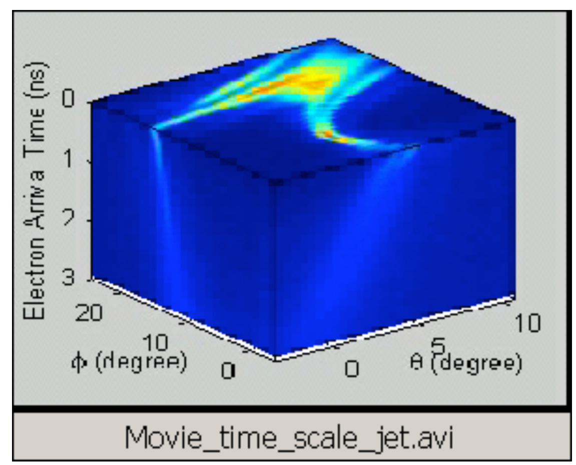
Currently used Hemispherical Analyzer (2D detection)

(Bi2212 Bi-layer splitting)



TOF Analyzer Proposed (3D detection)

(Bi2212 Bi-layer splitting)



Key Specifications:
Acceptance angle: 30 degree
Energy resolution: <=2meV (5eV Pass Energy)
Angular resolution: <=0.1 degree (~2mrad)
(comparable to Scienta analyzer but 100 times faster)

Fabrication – in progress

Time-Scale of Various Phenomena

- Ultra-fast time regime: $\leqslant$ 200fs (ΔE >10meV)
  - Electron excitation/de-excitation (fs)
  - Bond breaking
  - Carrier-carrier scattering
  - Hole-optical phonon scattering
  - Charge density wave/charge transfer
  - Magnetic Dynamics
  - Relaxation of biological system after light absorption (Rhodopsin);
- Time regime: ~ 200fs - 2ps (ΔE ~1-10 meV)
  - Phase transition (diamond $\longleftrightarrow$ graphite)
  - Carrier acoustic phonon scattering
- Time regime: > 1-100ps
  - Stripe fluctuation in High Temp Superconductor
  - Magnetic recording
  - Protein folding (ps-s)

meV Resolution Soft X-Ray Beamline (MERLIN)

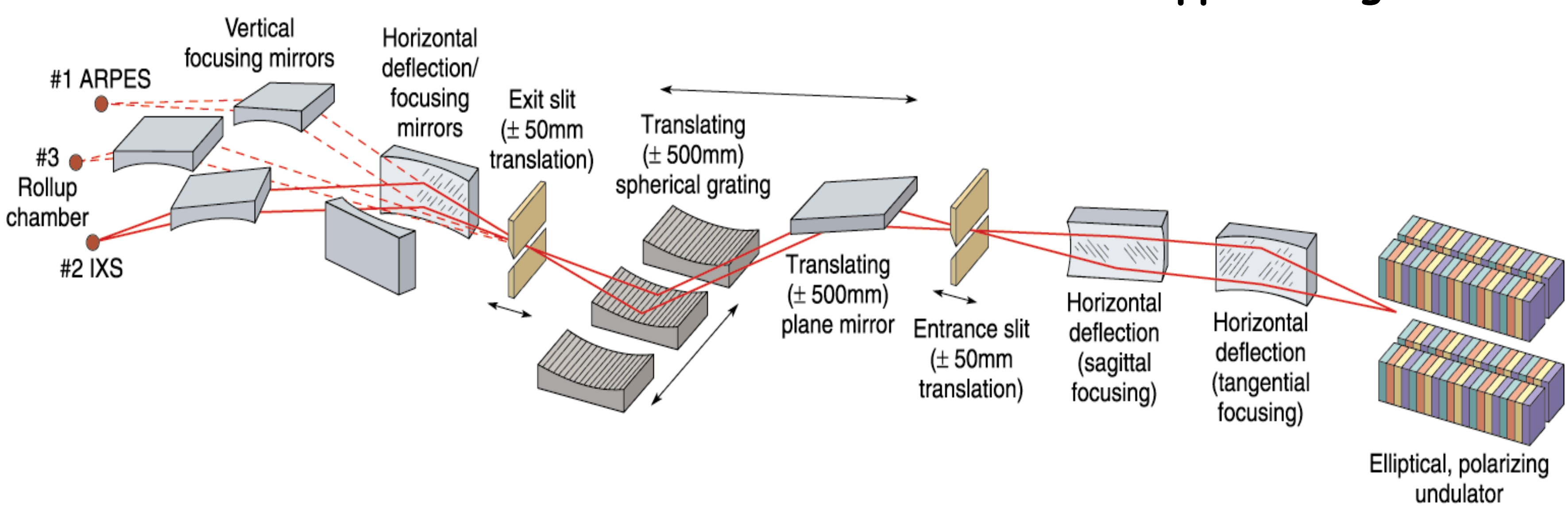
Specifications:

- Resolving power: E/ΔE=100,000 with 5μm slits
  i.e. better than 1 meV when photon energy is below 100eV
- Photon energy range: 15eV to 100eV, fully optimized
  maximum achievable photon energy ~140eV
- Elliptically Polarized Undulador (EPU): full polarization selection (linear and/or circular)
- Photon Flux: ~ 5 $\times 10^{11}$ photons/s/meV

Optical Layout (SGM)

✓Ultra High Resolution
& High Resolution Modes

✓ Asymmetric Undulator
to suppress higher orders



meV Resolution Spectroscopy (MERLIN) Beamline

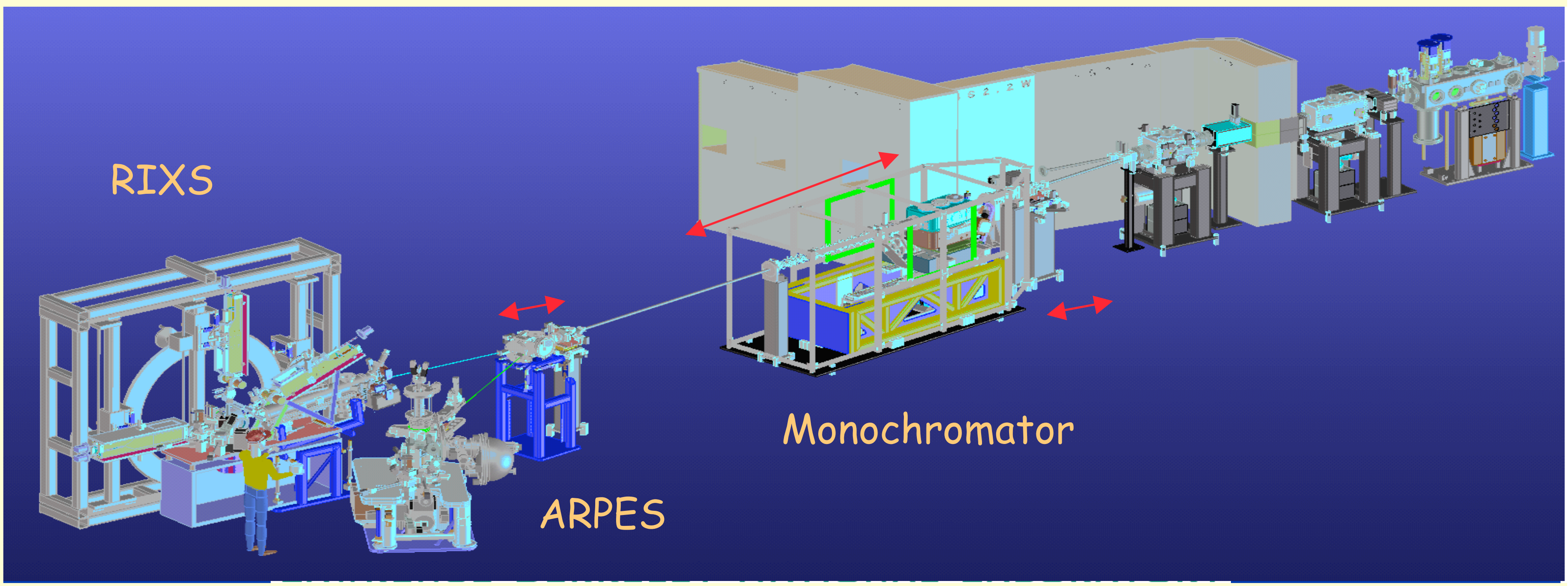
Specifications:

- Resolving power: E/ΔE=100,000 with 5μm slits
  i.e. better than 1 meV when photon energy is below 100eV
- Photon energy range: ~ 8eV to 100eV, fully optimized
  maximum achievable photon energy ~150eV
- Elliptically Polarized Undulador (EPU): full polarization selection (linear and/or circular)
- Photon Flux: ~ 5 ×10^{11} photons/s/meV

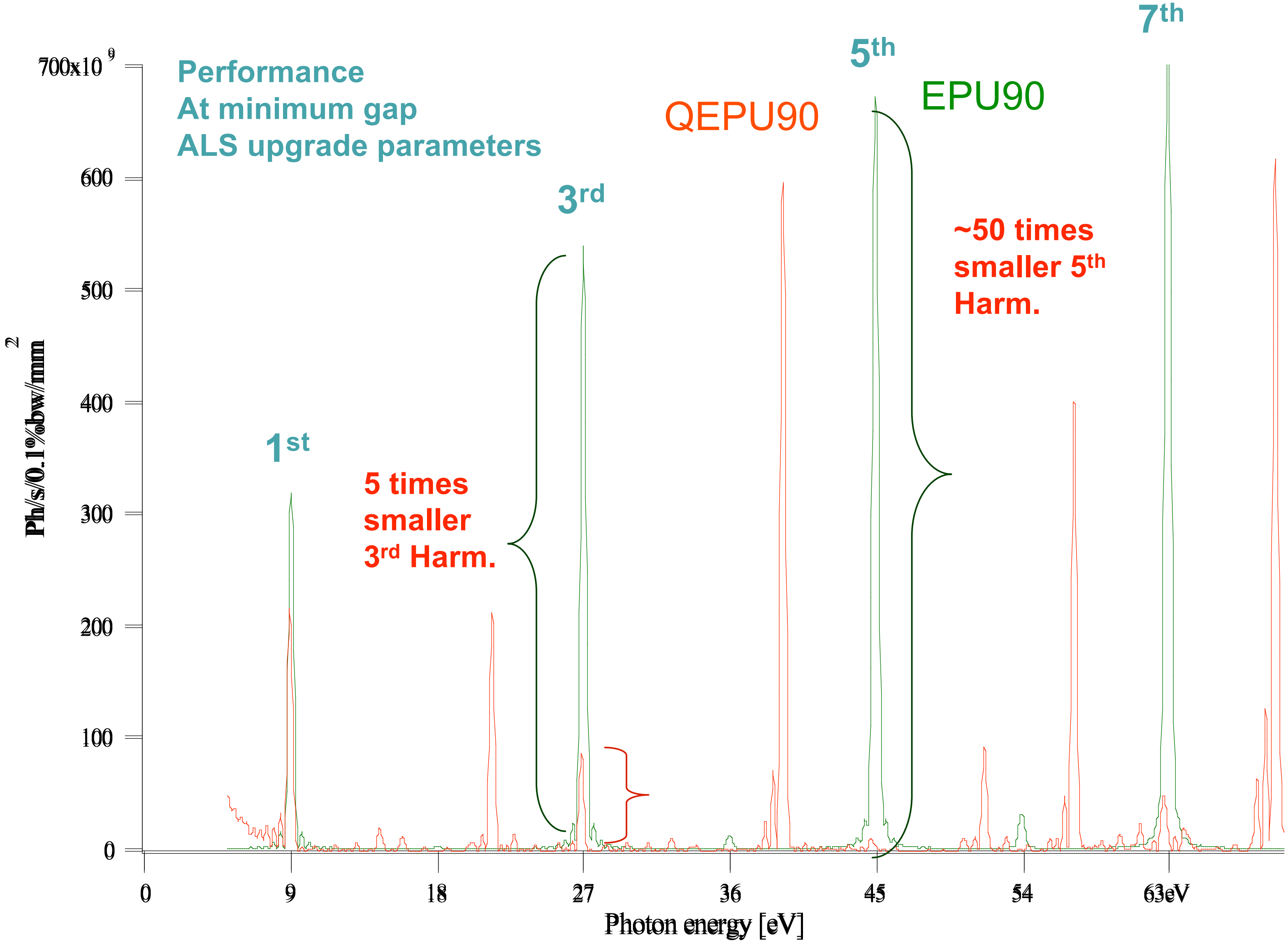
MERLIN Layout

Ultra-High Resolution & High Resolution Modes

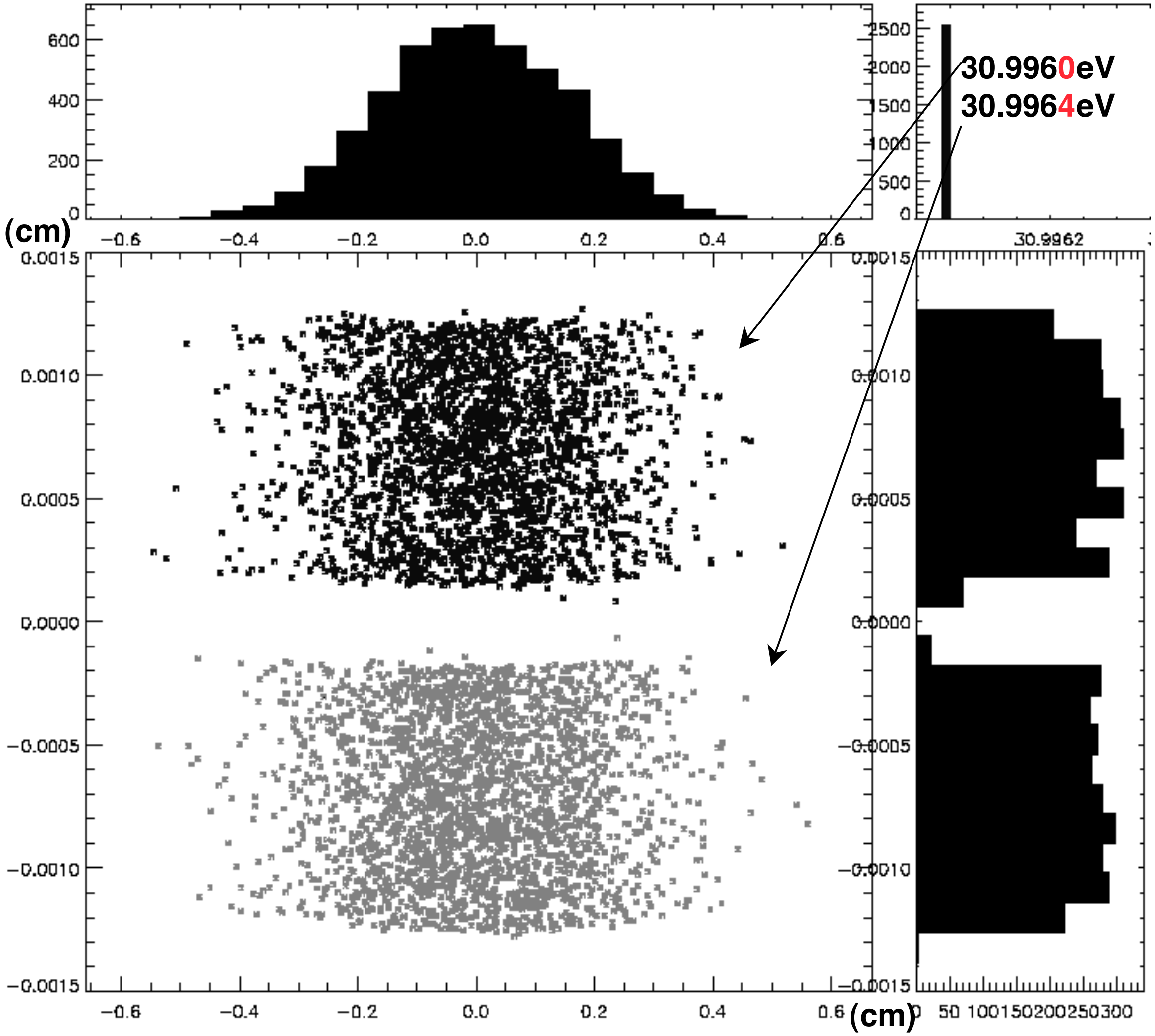
Quasi-periodic undulator for Higher order



Reduced Flux in Higher Harmonics



Ray Tracing (Shadow)



$h\nu \sim 30eV$

Groove density=1,800 l/mm

ΔE_{slit} = 0.029meV/μm

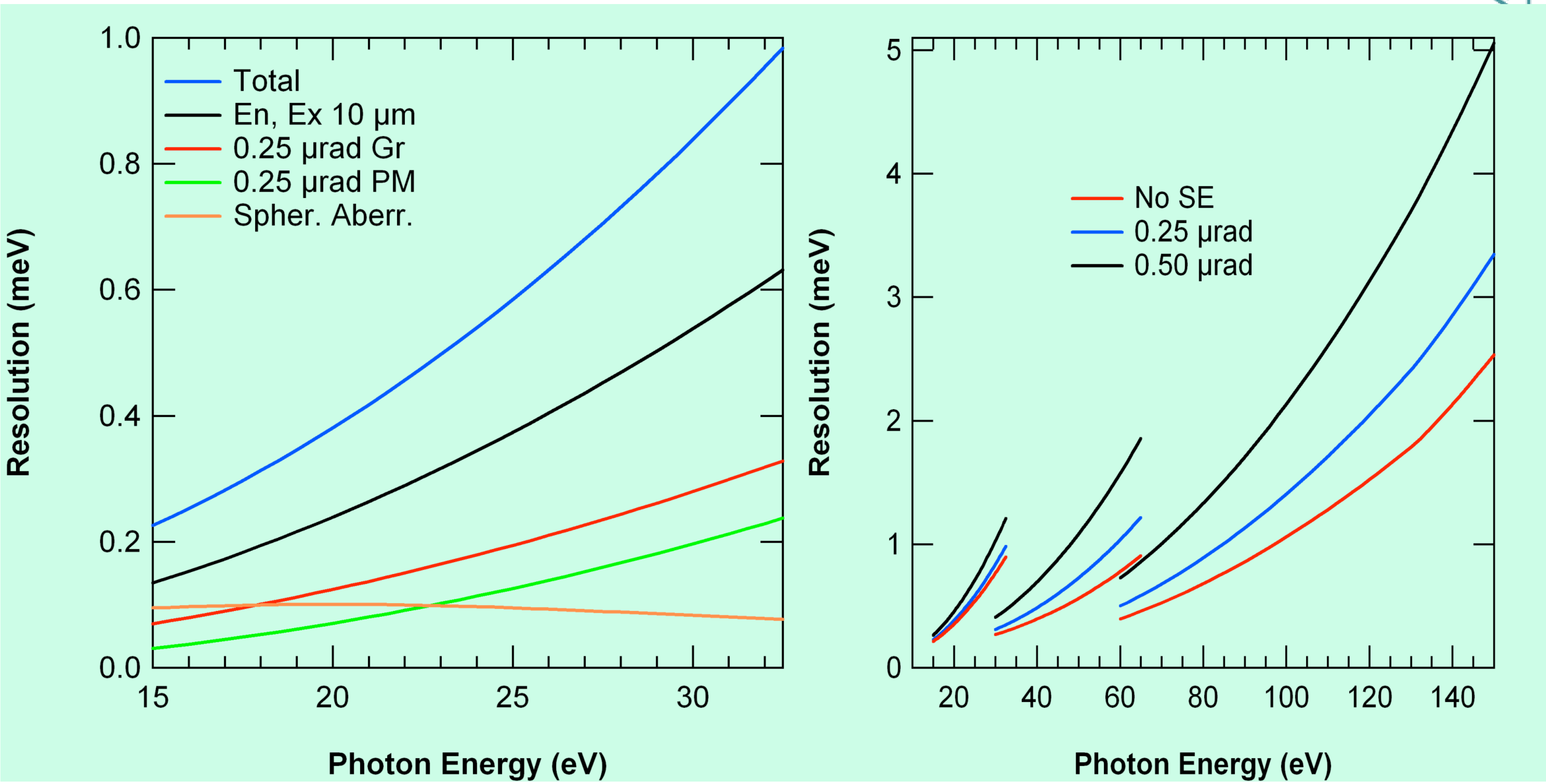
ΔE_{slope} = 0.22meV/μrad

ΔE_{slit}=0.14meV @ 5 μm slit

slope error (μrad)	0.25	0.50
ΔE_{slope} (meV)	0.055	0.11
$\Delta E_{tot}=(\Delta E_{slit}^2 + \Delta E_{slope}^2)^{1/2}$	0.15	0.18

Yi-De Chuang

Resolution Rowland Mode

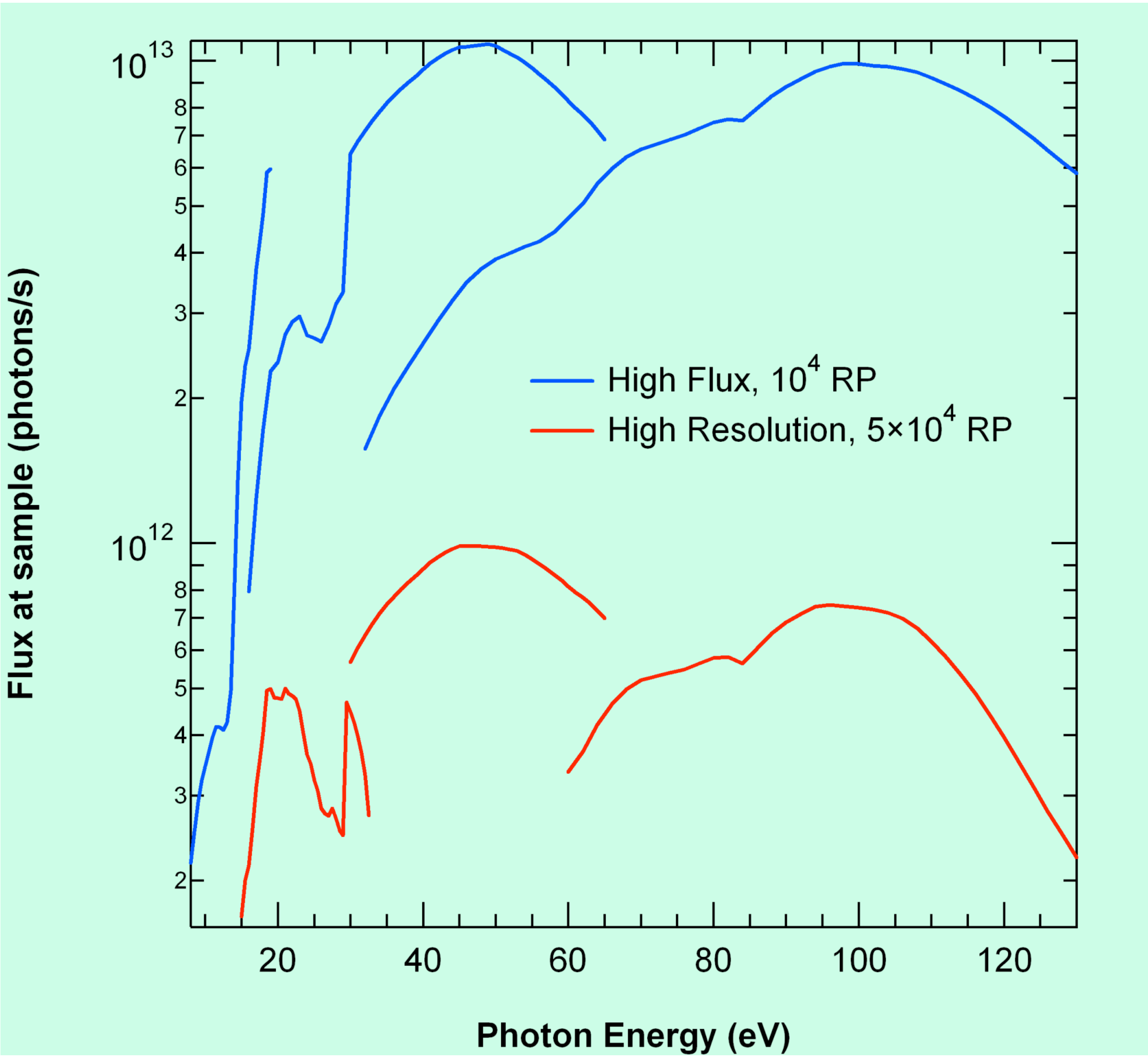


LEG: 900 l/mm

Defocus, coma = zero. Line curvature negligible.

LEG: 900 l/mm, 10µm slits
MEG: 1800 l/mm 5µm slits
HEG: 3600 l/mm, 5µm slit

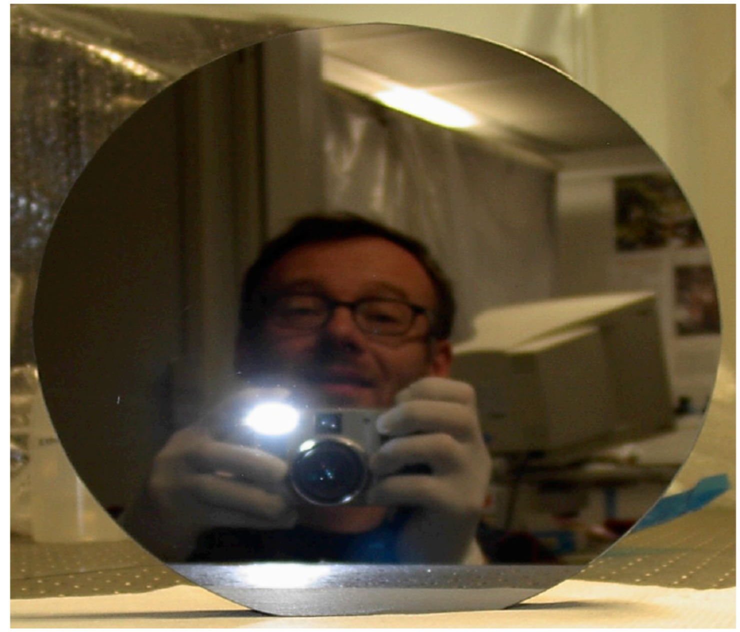
Flux @ sample



ID flux into 0.9×0.9 mrad^2
Transmission entrance slit
Reflectivity all mirrors
Grating efficiencies
Band width correction

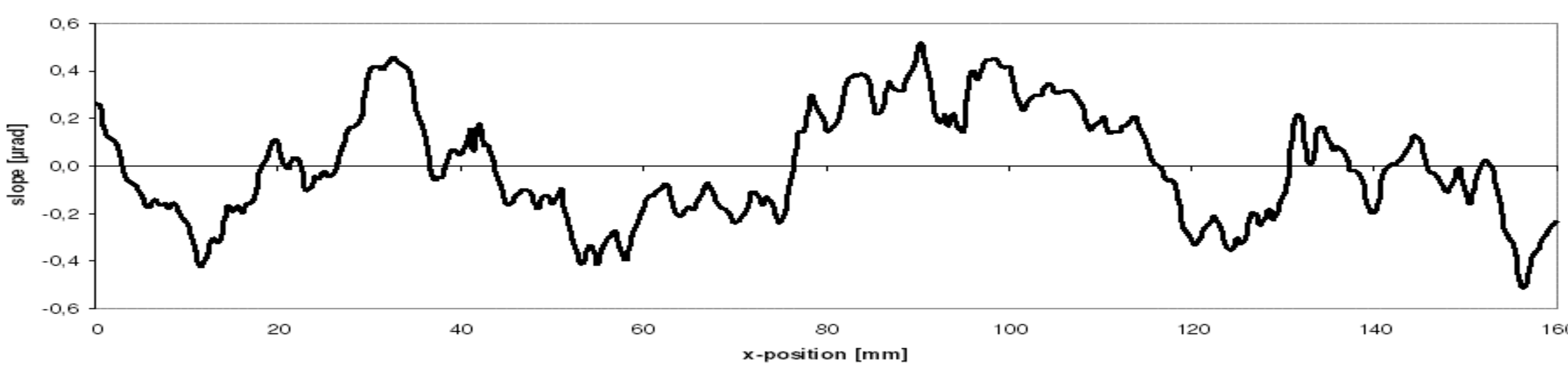
Cutting-edge technology spherical grating substrate

High resolution grating substrate (measured at BESSY metrology laboratory)



0.23μrad RMS slope error

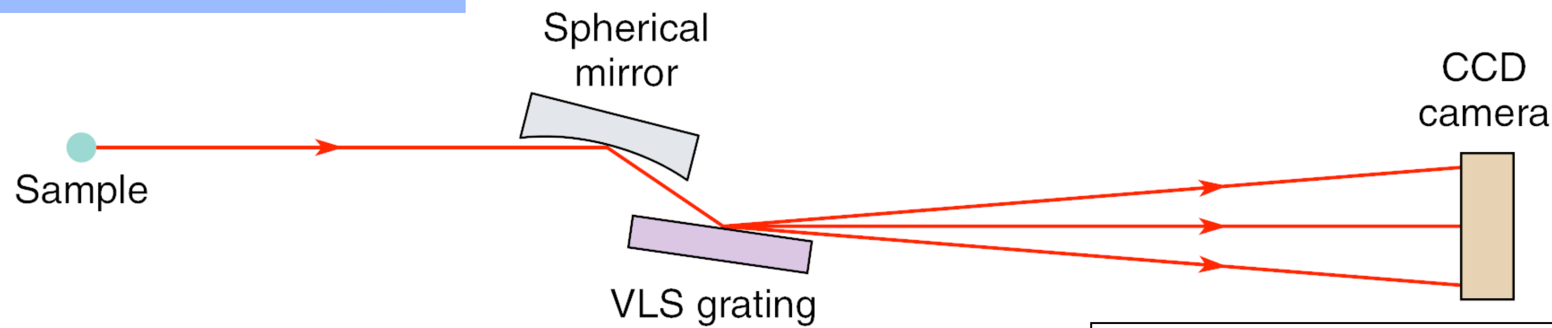
MERLIN R=15m, center line, profile of residual slope



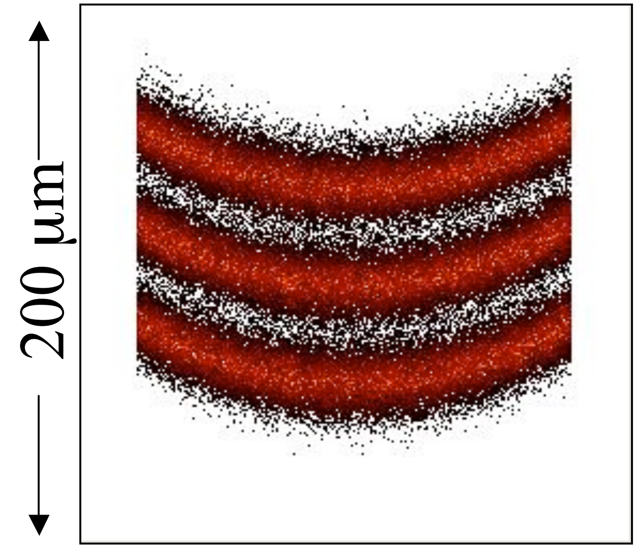
residual slope error: 1.03 μrad pv / **0.23 μrad rms**, radius of curvature: **14.965 m**

meV Resolution VLS Spectrograph

Optical Design



Ray Traces

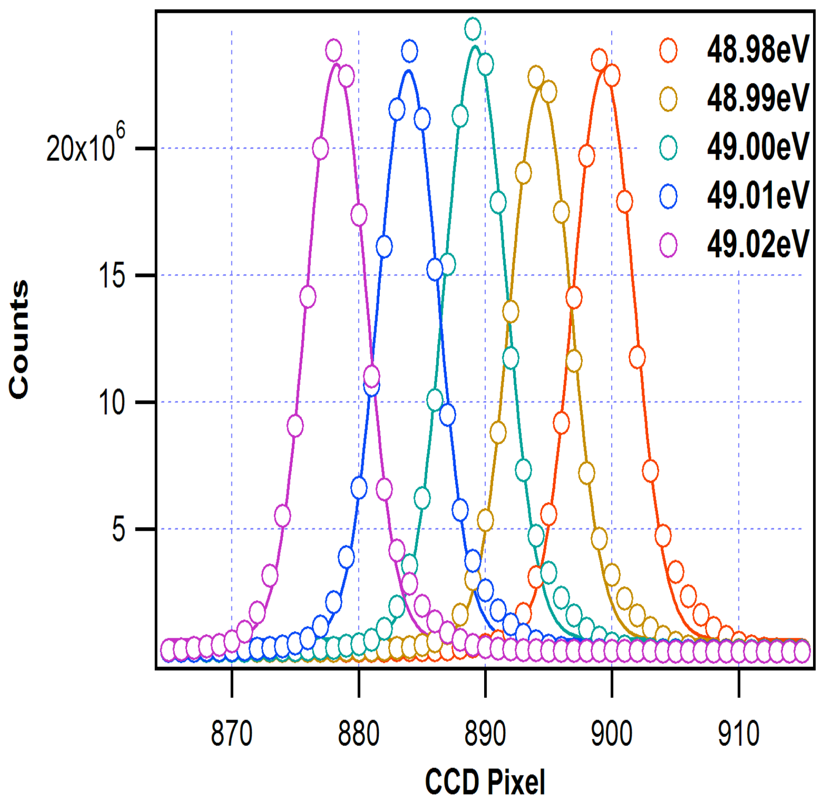


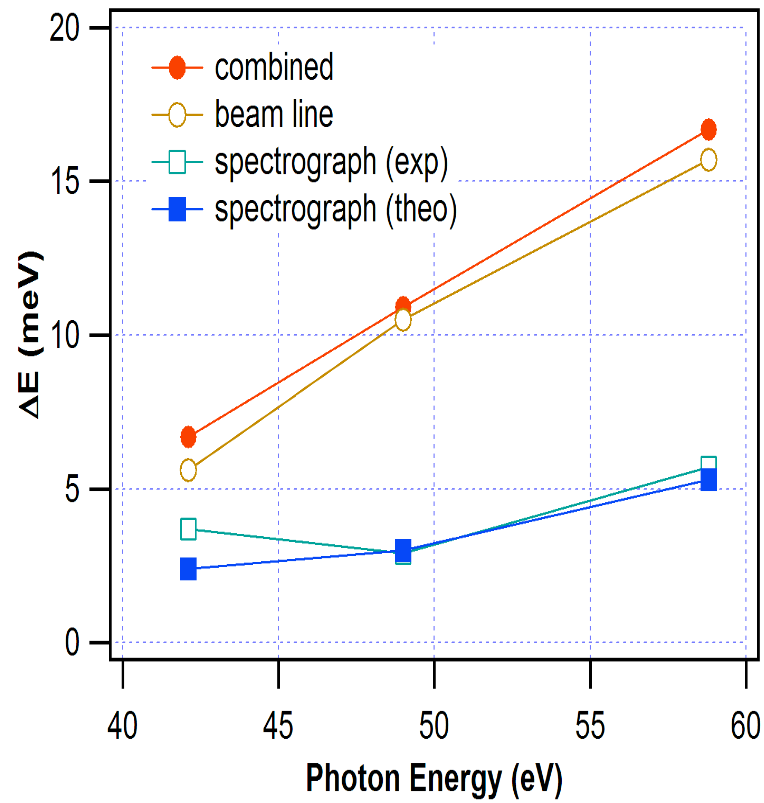
$h\nu = 49$ eV $\pm$ 5meV

- Calculated/measured Resolution
  3 meV (high efficiency)
- Overall length = 2 meters.
- Spectrograph for Merlin beamline
  (completion summer 2007)

Spectrograph: Energy Resolution Test

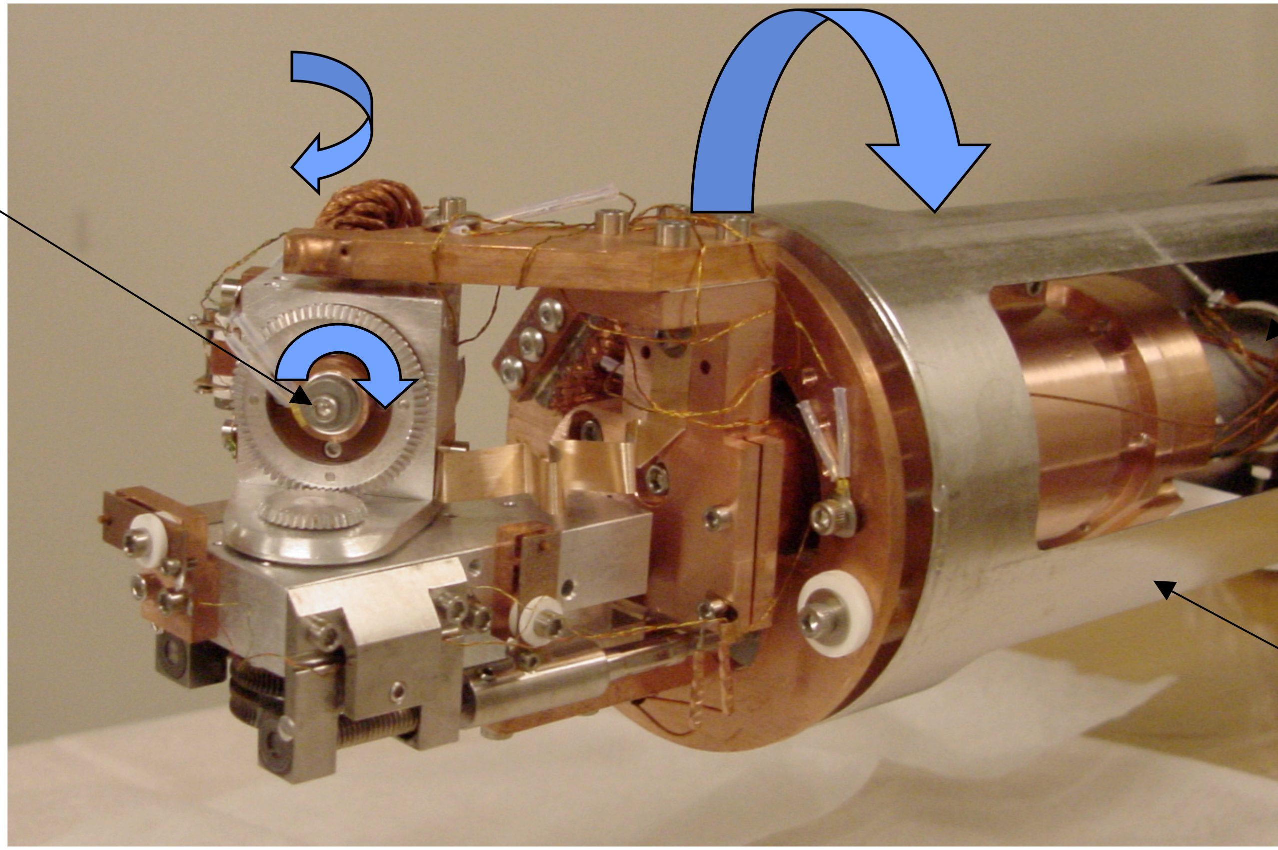
Straight beam with ~ 6μm source size BL 12.0





Low-Temperature Goniometer with Six Degrees of Freedom

Sample Position



Cryostat

Support tube

(1). Six degrees of freedom: 3 rotational and 3 translational;
(2). Samp temperature ~10 K (no radiation shield);
(3). Stability of sample against temperature change

Designed and fabricated by John Pepper (BL 10.0)

Acknowledgement

- **Photoemission:** Z X Shen (Stanford), Eli Rotenberg, (LBNL, ALS), Xingjiang Zhou (ALS, China), Wanli Yang (ALS),Norman Mannella (ALS, Stanford), Simon Mun (ALS), Akira (NSLS)
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